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SOIL SCIENCE AND SEMANTICS

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GRAMMAR is concerned with the relationship of words and the construction of sentences. Whether or not a combination of sentences produces a valid statement lies outside the realm of grammar. 'I do not like oranges, but my uncle, who is on the shores of the Mediterranean Sea, also does not speak French,' is a grammatically correct yet completely meaningless example from an old-fashioned textbook. The relationship between sentences as assertions is treated in logic. Logic, however, accepts arbitrary definitions of key-words as the basis of assertions, and hence assertions need not necessarily bear any relation to the world of fact.

Semantics is the science of meanings, as contrasted with phonetics, the science of sounds; it goes further than logic and deals not only with validity, words, and assertions but also with the truth. Moreover, semantics evaluates the effect of words upon human behaviour. It considers the chain: 'fact to nervous system to language to nervous system to action'.

At present semantics plays an increasingly important role in phenomenological psychology, psychiatry, and cultural anthropology (Rapoport, 1952). We are told that language affects the activity of scientists, and the limitations of language tend to divert scientific work away from Aristotelian principles. Both commercial and political demagogy aims to channelize the reactions of people to symbols in order to promote the sale of inferior products or to incite hostilities between different groups of people. The essentials of semantics in a popularized form are summarized in Chase's *Tyranny of Words* and Hayakawa's *Language in Action*.

There is indisputable evidence that semantics exerts a strong influence on the development of certain branches of soil science, particularly soil genesis. For nearly half a century, pedologists have been living and working not in a world of realities, but in a realm replete with hypnotizing emanations of words or symbols.

Let us consider the well-established term 'podzol'. Originally it was meant to designate sesquioxide-impoverished raw-humus soils found in boreal regions and characterized by the ashy-grey colour of their eluvial horizons. At present this term confuses the climatic-zonal classification of soils of five continents and paralyses the constructive thinking and action of pedologists. As often as not, pedological ignorance, unavoidable in the infantile stages of this scientific branch, is covered up by the use of one or another variation of the word 'podzol'.

Podzolization is a very specific process, but this word is often used as if it were synonymous with 'leaching', a phenomenon common to a great variety of soils. Thus the true genetic nature of many soils is obscured

by a smoke screen of such terms as 'weakly podzolized soils', 'grey-brown podzolic soils', 'crypto- or phanero-podzolic soils', 'latent podzols', 'podzolized brown earths', 'podzolized lateritic soils', 'yellow podzolic soils', 'red podzolic soils', and 'brown podzolic soils'. Some of these soils cannot be classed among podzolic soils even by a long stretch of the imagination, since they are formed under essentially different climatic and floristic conditions and show distinctly different morphology. A quotation from the work of Stephens (1950, p. 127) is one of many that corroborates the above statement:

> In Australia, where the forest and shrub vegetation is almost entirely of a sclerophyll character with litter fall slow and relatively continuous, and where the podzolic soils extend into areas where grass species are widely present, the A_{00} has a different character. . . . In North America and Europe the horizon of organic decomposition —the A_0—is invariably present: it may be as little as $\frac{1}{2}$ in. thick. In Australia it has not been recorded under natural conditions. It is certainly absent in all but the rain-forest areas: it may occur there, but no published descriptions of podzols and podzolic soils indicate its presence. . . . In Australia the A_1 is generally thick, frequently more than 6 in. . . .

Thus Stephens gives a very comprehensive and elucidating description of Australian soils common to warm and humid regions of leather-leaf forest. He objectively observes that 'It would, indeed, be surprising if the organic horizons of Australian podzols and podzolic soils were identical with those of the northern hemisphere. . . .' Now, would it not be in the interest of science and reduction of confusion to leave the term 'podzolic' unmolested and call Australian soils of sclerophyll forest by another name selected from the wealth of English, Latin, or native vocabularies?

The same problem of terminology was touched upon by the late Professor G. W. Robinson (1950), who suggested that:

> At present a number of terms are in common use and it is unlikely that a given term, e.g. podzol, is always used in the same sense. It may even be that individual authors themselves may not be quite clear as to the precise meaning they attach to their terms. If, as the writer holds, the terms in use represent not real universals like the species and genera of animals and plants, but complexes of characteristics or constructed universals, then it is of the highest importance that cooperative effort should be directed towards definition (p. 155).

Some 70 years ago Dokuchaev (1879) enriched pedological nomenclature by a descriptive folk term—chernozem, meaning 'black earth'. At a later date Dokuchaev's followers added a few coined imitations of the folk terminology—sierozem, krasnozem, and burozem, meaning 'grey earth', 'red earth', and 'brown earth'. Still later, Ramann (1918) baptized the forest soils of central Europe with the name 'Braunerde', a translation of burozem, the Russian expression for semi-desert soils. This was done without analysis of a single soil profile (Stremme, 1930) and contributed little except for the introduction of a rather enigmatic concept. Subsequently different authors applied the designation 'Ramann's brown earth' to a range of soil groups of widely different origin, including weakly podzolized soils, grey-brown podzolic soils,

mull soils of calcareous and non-calcareous substrata, certain varieties of rendzinas, soils of lateritic make-up, and even degraded chernozems (Glinka, 1931). The fact that the brown earths are not always of a brown colour did not help to make things better.

The misinterpretation of the genetic nature of some central European soils was a rather embarrassing experience, but it bore no ill consequences in the geographic and agro-silvicultural milieu of that region. The disaster resulted from the later misuse of the word 'brown' and from the gradual replacement of simple and expressive pedological nomenclature by a highly conventional designation of soils on the basis of colour.

The brown pigment alone gave rise to the following designations: 'brown earth' or 'brown forest soils', 'brown non-forest soils' or 'burozems', 'grey-brown podzolic soils', 'grey-brown calcareous desert soils', 'grey-brown forest soils', 'brown podzolic soils', 'subarctic brown forest soils', 'podzolized brown earths', 'non-calcic brown soils', 'solonized brown soils', 'yellowish-brown lateritic soils', 'reddish-brown lateritic soils', and 'brunigra soils'. And this is but one segment of the entire 'terminological spectrum' of modern pedology!

Strangely enough, this utterly bewildering spectographic array owes its existence largely to the members of the two language families that produced Shakespeare and Pushkin in literature, and Dokuchaev and Hilgard in soil science.

What is the reason that pedologists compare so unfavourably in regard to nomenclature with botanists, chemists, and especially with men of the medical profession? Is it wholly because of their lack of cultural background, scientific training, or imagination? Certainly not, for nearly any issue of a periodical devoted to soil science proves beyond any shadow of a doubt that soil scientists are as capable and brilliant as their colleagues in other fields of scientific endeavour. Sufficient it is to mention the achievements of soil specialists in colloidal chemistry, plant nutrition, and antibiotics. Most likely the answer lies in the so-called 'neurolinguistic aspects' and 'signal reactions' dealt with in semantics: the hypnotic effect of words.

'Podzolic' and 'brown' are two accepted and oft-repeated terms in soil genesis, and psychophonetic pressure forces a man of a high intellect and ability to bring into the world the designation 'brown podzolic soils', an ambiguous 'white-blackbird' concoction, meaning, in a literal translation, 'brown soils of an ashy-grey colour'.

Be that as it may, the existing terminological situation in soil science is well expressed by the French saying, 'Ce qui est trop ne vaut rien.' The variations on the same podzolic-red-yellow-brown theme are definitely overplayed and the coda is long overdue. Students of soil genesis will do well to seek new horizons for suitable terminology. They should discard the jumbled verbal kaleidoscope and turn to simple folk terms as are occasionally found in pedological reports. Patana soils of Ceylon, badob soils of Sudan, regur of India, muskeg of North America, and smonitsa of Yugoslavia are a few examples of words that are brief and phonetic, that possess inherent individuality, and carry the flavour of the land that brought them into existence.

Acknowledgements

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A STUDY OF PODZOLIZATION

PART I. THE MOBILIZATION OF IRON AND ALUMINIUM BY SCOTS PINE NEEDLES

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THE process of podzolization has long been the subject of experiment and conjecture, and many different mechanisms have been proposed to account for the mobilization and subsequent reprecipitation of the ferric and aluminium oxides in podzolized soils.

Broadly speaking the various suggested mechanisms fall into two classes; according to the first, and probably more widely held theory, the free oxides are transported as humus- or silica-protected sols, while according to the second hypothesis the iron and aluminium move in the form of soluble metal-organic compounds. Obviously very different mechanisms will be required by these theories to account for the reprecipitation of the sesquioxides.

Aarnio (1913) studied the mutual precipitation of humus and ferric or aluminium sols, and more recently Deb (1949) has found that by using more dilute preparations relatively greater amounts of the sesquioxides may be stabilized by the humus sol.

Morison and Sothers (1914) suggested that the deposition of ferric oxide in iron pans is due to irreversible precipitation from humus-protected sols during periods of drought, while the very exhaustive work of Mattson has been based on the assumption that reprecipitation of the oxides in the soil takes place in the horizon at which the isoelectric point of the sol is achieved. Van Schuylenborgh (1950), however, has obtained very different values from those generally accepted for the isoelectric points, having prepared his oxides by slow precipitation from very dilute systems.

The alternative view that translocation of sesquioxides occurs in the form of complex organic compounds was adopted by Jones and Wilcox (1929) who, on the basis of laboratory experiments, postulated that hydroxy acids are responsible for the solution of the free oxides, the iron and aluminium being translocated as complex anions and subsequently precipitated as basic salts. Gallagher and Walsh (1943) studied the solubilities of the organic matter and sesquioxides of podzolized soils in oxalic-acid solution. Consideration of the results, in the light of the measured capacities of the various horizons to absorb organic matter from solution, led them to conclude that translocation of sesquioxides is effected prior to that of the organic matter. They were therefore of the opinion that movement of the iron and aluminium is caused by the solvent action of simple decomposable acids, of which oxalic acid may be regarded as the type. Halvorson and Starkey (1927) came to a similar conclusion on the basis of their work on the solution of ferric oxide in the

presence of fermenting sugars. These investigators suggest that reprecipitation is caused by assimilation of organic ligands by continued microbial action during percolation of the dissolved complexes down the profile.

The presence of raw humus or peaty organic matter is generally considered to be an essential factor in the process of podzol formation (e.g. Robinson, 1949), and presumably for this reason much of the earlier work has been based on the assumption that peat is the active agent in the translocation of the free oxides. It has been shown, however, that in comparison with fresh plant material and under anaerobic conditions peat is relatively ineffective in causing dissolution of ferric oxide (Bloomfield, 1951). While it is not known how far the behaviour of the peat was modified by the drying to which it had been subjected, from the very fact of its persistence, it seems that the peat must represent a relatively inert fraction of the original plant material, and it is probable that the plant material which does not remain in the peat residue exerts a greater influence in mobilizing iron and aluminium. This paper describes the results of an investigation of the properties of aqueous extracts of pine needles.

Experimental

Scots pine needles, dried at 60–70° C. and ground to a fine powder in a Raymond mill were used throughout this work.

pH of aqueous extract. Five grammes of the air-dry ground needles were extracted overnight with cold distilled water, filtered, and the filtrate diluted to 200 ml. The pH of the extract was 3·9.

Steam distillation of the extract after acidification with dilute sulphuric acid gave essentially no separation of volatile acids. Electrometric titration of the extract with alkali gave a titre equivalent to 0·17 milli-equivalents of acid per gramme of the air-dry needles.

Solution of ferric and aluminium oxides. Five grammes of ground pine needles were shaken for 4–5 hours with cold distilled water, filtered, and the filtrate and washings made up to 100 ml. The extract was added to *c.* 0·1 g. of co-precipitated ferric and aluminium hydrous oxides. The reaction mixture was contained in a glass reagent bottle of 250-ml. capacity, and no attempt was made to exclude oxygen during the reaction. A few drops of toluene were added to prevent mould growth and the mixture was kept in an incubator at 27° C., with occasional shaking. Samples were withdrawn periodically and, after centrifuging, the dissolved iron and aluminium were determined absorptiometrically, using $\alpha\alpha'$-dipyridyl and aluminon respectively, after destruction of organic matter by digestion with nitric/perchloric/sulphuric acid. The results, illustrated in Fig. 1, show that the solvent action is very great. A more surprising result, however, was the discovery that a large part of the dissolved iron was in the ferrous state, as shown by testing with $\alpha\alpha'$-dipyridyl. By treating an aliquot of the centrifuged reaction mixture with a small amount of ferric-chloride solution it was found that the pine extract still possessed a considerable capacity to reduce soluble ferric iron. The following results refer to the reaction mixture after 25 days' contact with ferric-aluminium oxide:

Total dissolved iron	0·30	mg. per g. pine needles.
Ferrous iron	0·13	" "
Residual reducing capacity	6·89	" "

Since the residual reducing capacity of the reaction mixture exceeds the total dissolved iron by such a large factor, it is unlikely that the difference between the total and the dipyridyl ferrous iron contents represents iron present in the ferric state—certainly not in ionic form. It seems more probable that this difference represents ferrous iron present in a complex form which is too stable to react completely with αα′-dipyridyl, in which case the 'pine complex' would be one of remarkable stability.

Effect of pH and aeration on solution of ferric and aluminium oxides. In the following experiment the effects of increasing the pH of the reaction mixture and of maintaining the system in an atmosphere of nitrogen were investigated.

The anaerobic experiments were carried out in filter-flasks fitted with delivery tubes through which samples could be expelled; suspended ferric aluminium oxide particles were retained by cotton-wool plugs fitted to the lower ends of the tubes. The flasks were swept out periodically with nitrogen introduced through the delivery tubes, which were provided with glass stopcocks. The aerobic reactions were carried out in partly filled reagent bottles as described in the previous section. The experiments were duplicated, using in one case an untreated pine needle extract, pH 4·2, and in the second series an extract previously adjusted to pH 7 by addition of sodium hydroxide.

The results are shown in Fig. 2, from which it can be seen that the extent of solution is decreased by increasing the pH of the system, and that this effect is most pronounced under aerobic conditions. In the anaerobic system, raising the pH to 7 does not cause a very marked decrease in the extent of solution, so that the process is obviously not governed by the hydrogen-ion concentration. The marked decrease in solution taking place under aerobic conditions at the higher pH, however, shows that oxidation effects can play an important role. That the presence of oxygen should have such a marked inhibitory effect on the solution of aluminium at the higher pH is surprising. A possible explanation is that the solution of a smaller amount of ferric oxide, in the presence of oxygen, causes the exposure of a smaller surface of alumina to the action of the pine extract.

Perhaps the most significant aspect of these results is that although the extent of solution of both ferric and aluminium oxide is reduced considerably at pH 7 in the aerobic experiments, it is nevertheless still appreciable; even at pH 7 the solution contained appreciable amounts of ferrous iron capable of reacting with dipyridyl. The figures given below refer to the two aerobic experiments after a reaction period of 25 days.

pH	4·2	7·0	
Total iron	37·1	26·3	mg./100 g. pine needles.
Ferrous iron	19·1	9·8	" "

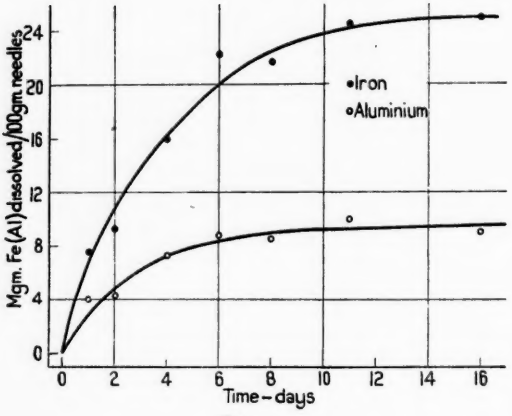
Mgm. Fe (Al) dissolved/100gm. needles
0
4
8
12
16
20
24
0
2
4
6
8
10
12
14
16
Time – days
•Iron
○Aluminium

FIG. 1.

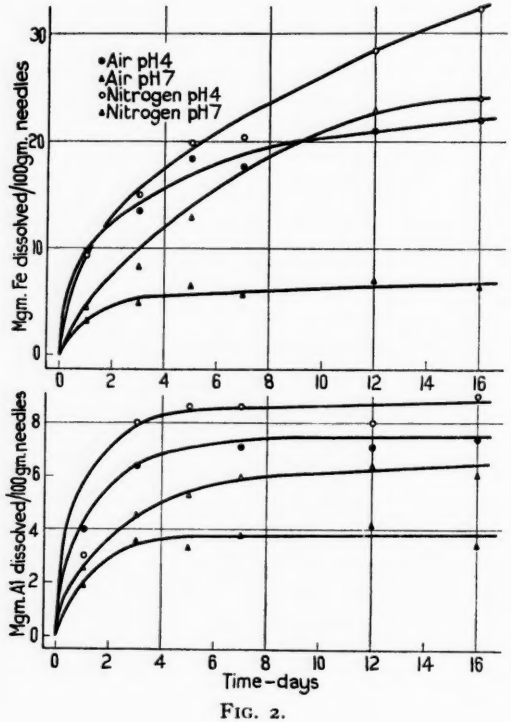
Mgm. Fe dissolved/100gm. needles
0
10
20
30
•Air pH4
▲Air pH7
○Nitrogen pH4
△Nitrogen pH7
Mgm. Al dissolved/100gm. needles
0
2
4
6
8
0
2
4
6
8
10
12
14
16
Time – days

FIG. 2.

As will be seen in the next section, the true ferrous contents of these solutions is probably higher than the values quoted.

Formation of stable ferrous complexes. Attention has already been drawn to the fact that in the solution resulting from the treatment of ferric oxide with an aqueous pine extract the total iron exceeds the ferrous iron, as determined by dipyridyl, by a fairly large factor. In order to determine whether this discrepancy results from the formation of a ferrous complex too stable to be capable of reacting completely with $\alpha\alpha'$-dipyridyl, the following experiment was carried out. Equal volumes of a pine extract were treated with increasing volumes of ferrous-sulphate

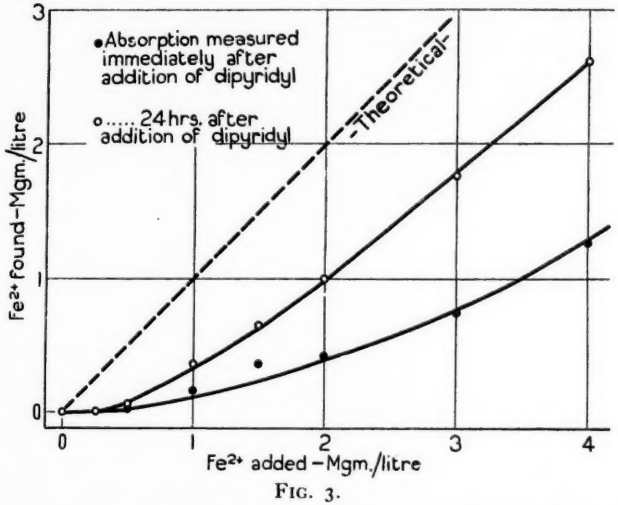

FIG. 3.

solution, and the apparent ferrous content was determined with dipyridyl in the usual manner. It was found that if the dipyridyl were added immediately after mixing the pine extract and ferrous solutions, a theoretical recovery of the latter was obtained. If, however, the mixture was left overnight before development of the ferrous-dipyridyl colour, an appreciable discrepancy appeared, as may be seen by reference to Fig. 3, in which the ferrous iron found is plotted against the amount added. It is readily seen that little or no ferrous reaction was obtained until a certain value for the added iron was reached, from which point the curve rises, eventually becoming approximately parallel to the theoretical curve. The experimental results are thus consistent with the formation of a complex stable to the action of the dipyridyl reagent; the break in the curve presumably corresponds to the point at which the stable complex-forming capacity of the pine extract is exceeded.

Fig. 3 also illustrates the effect of allowing equilibrium to be attained between the dipyridyl- and pine extract-ferrous complexes.

Existence of stable ferric complexes. In order to determine whether the aqueous pine extract is capable of forming a ferric complex which resists

reduction, the following experiment was carried out: 5-ml. portions of a 10 per cent. pine-needle extract were treated with measured volumes of a solution of ferric ammonium sulphate, the amount of ferric iron added being considerably less than the reducing capacity of the pine extract. The mixtures were kept in the dark for 72 hours to ensure complete reduction, after which the ferrous iron was determined in the usual manner. These values were corrected for the unreactive ferrous iron, using the results obtained in the previous experiment, and the measured and theoretical values compared. In the event of stable ferric compounds being formed, the measured iron contents should be less than theoretical values, and it was found that for very small amounts of ferric iron the experimental and theoretical values were in close agreement, suggesting that no stable ferric complexes are formed. For higher amounts of ferric iron, however, a secondary effect vitiated the results; under these conditions a dark purple-coloured compound was formed, presumably between ferrous iron and oxidation products of the pine extract, which was strongly absorbing in the region of maximum absorption for ferrous dipyridyl, and which was not completely decomposed in the presence of the dipyridyl reagent. High results were therefore obtained.

Although the results of this experiment are less conclusive than could be desired, it seems reasonably certain that in the presence of an excess of pine reducing compounds, ferric iron is completely reduced to the ferrous state.

Rate of stable complex formation. It is apparent from the preceding sections that formation of the stable complex takes a measurable time for completion. In order to obtain an indication of the rate at which this takes place, 50 ml. of a 20 per cent. pine-needle extract were added to 50 ml. of a solution of ferrous sulphate, containing 20 mg. of iron per litre, and the mixture kept in the dark. Portions were pipetted off at intervals, treated with dipyridyl reagent, and the absorption measured immediately in order to minimize displacement of the equilibrium point by the dipyridyl. Blank determinations on the ferrous solution showed that oxidation effects were negligible. The results are shown graphically in Fig. 4, from which it can be seen that the stable complex formation is virtually complete after approximately 20 hours. When the iron is derived from solid ferric oxide, formation of the complex presumably keeps pace with the solution and reduction of the oxide until the particular ligand is exhausted.

Rate of reduction of ferric iron. In order to determine the rate at which reduction of dissolved ferric iron takes place in the presence of an aqueous pine extract, 5 g. of needles were extracted with 100 ml. of cold water as before; 10 ml. of the extract were pipetted into a 200-ml. flask together with 20 ml. of N/80 ferric ammonium sulphate solution. After dilution to volume the mixture was kept in the dark, aliquots being removed at intervals for determination of ferrous iron, using dipyridyl. It can be seen from Fig. 5 that although appreciable reduction takes place in the first few minutes, the reaction takes much longer to achieve virtual completion. It follows from the preceding section that these

results give slightly low values for the reduction, since no correction has been applied for the ferrous iron which was not returned by the dipyridyl reagent.

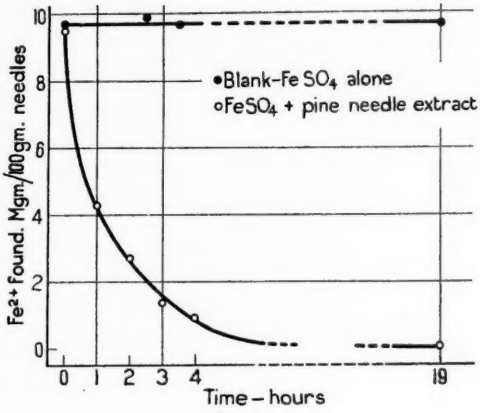

FIG. 4.

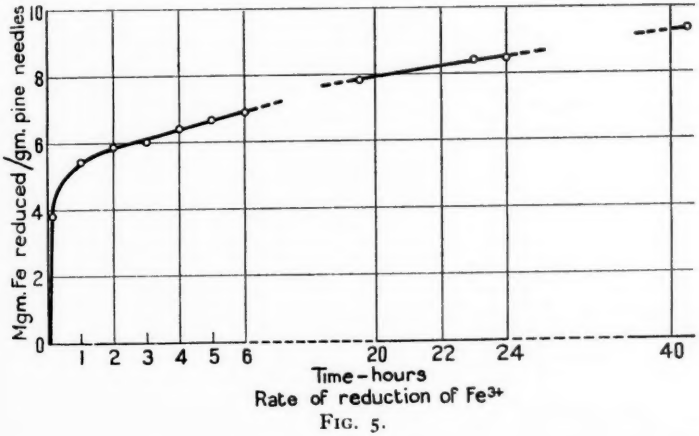

FIG. 5.

Effect of aeration on the reducing properties of aqueous pine extracts. A knowledge of the effect of atmospheric oxidation on the reducing capacity of an aqueous pine-needle extract is desirable, not only from a direct pedological viewpoint, but also for the light which such information would throw upon the mechanism of the reduction of ferric iron. In order to investigate the rate of oxidation, a 5 per cent. aqueous pine-needle extract was prepared and divided into two parts. One portion was treated with dilute sodium hydroxide solution to give a pH of 7·2,

the other being left untreated at pH 4·3. The two extracts were then treated with a few drops of toluene and shaken in partly filled reagent bottles. The reducing capacities of the extracts were determined periodically as follows: 5 ml. of the extract were pipetted into a 100-ml. graduated flask and treated with 10 ml. of N/80 ferric ammonium sulphate solution. The mixture was left in the dark for 48 hours to allow completion of the reduction, and then treated with dipyridyl reagent and ammonium acetate buffer in the usual manner. Measurement of the absorption was made after standing for a further 24 hours in order to allow equilibrium between the pine- and dipyridyl-ferrous complexes to be attained. It will be obvious in the light of the preceding discussion that the values obtained by this method are less than the true reducing capacities by an amount equal to the dipyridyl-stable ferrous complex formed by the pine-needle extract.

TABLE 1

Time (days)	*Reducing capacity mg.* Fe^{3+} *reduced/g. air-dry pine needles*	
	pH 4·3	*pH* 7·2
0	9·1	7·7
1	8·9	7·7
12	9·8	8·3
18	9·1	7·1
26	9·1	7·8
33	9·7	7·1

As may be seen from Table 1, this method is not capable of giving very precise results and it is not possible, therefore, to decide whether the reducing capacity does in fact decrease on aeration of the extracts. It seems certain, however, that if a decrease in the reducing capacity occurs, it is at a very much slower rate than that of the reduction of ferric ions by the extracts. It follows, therefore, that since the reducing compounds are relatively inert to the action of atmospheric oxygen, they are unlikely to be capable of reducing ionic ferric iron, and that the reduction is probably preceded by the formation of a ferric complex.

Reoxidation of ferrous-pine-extract complex solution. Since the ferrous solutions obtained by treating ferric oxide with a pine-needle extract have been shown to retain extensive residual reducing properties, the ferrous solutions used for this work were prepared as follows: 50 ml. of a 5 per cent. pine-needle extract were treated with 50 ml. of N/80 ferric ammonium sulphate solution and, after the addition of toluene, were left in the dark for 48 hours to allow complete reduction. Having thus satisfied the Fe^{3+} reducing properties of the extract, the mixture was centrifuged and divided into two parts to which dilute sodium hydroxide was added to give pH values of 4·3 and 7·6 respectively. The fact that no precipitate was formed in either case can be taken as proof of the complex nature of the ferrous compounds present. The ferrous solutions

were then shaken with air as in the previous experiment, and the ferrous and total iron contents of the solution determined periodically.

The results, given in Fig. 6, show that at pH 4·3 oxidation results in an approximately parallel decrease of both the total and the (dipyridyl) ferrous iron contents; the difference between the total and ferrous contents most probably represents the dipyridyl-stable ferrous complex, in which case it is possible to say that in the region of pH 4 oxidation is

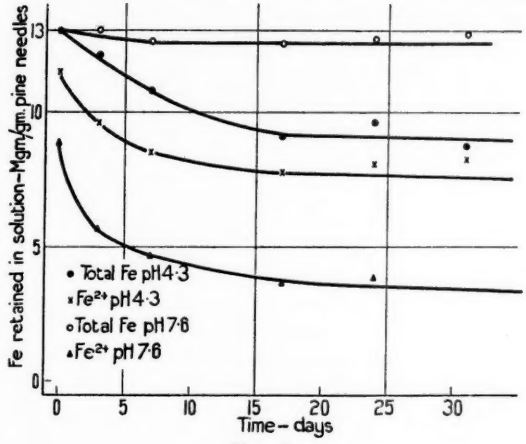

FIG. 6.

accompanied by precipitation of all the oxidation products. At the higher pH, however, it is clear that a quite different mechanism is operative. In this case the total iron scarcely decreases, while the ferrous iron decreases comparatively rapidly; the difference between the total and ferrous figures grows much larger as the time increases. The decrease in the concentration of ferrous iron shows that appreciable amounts of iron are oxidized, but very little iron is precipitated, as is evident from the comparative constancy of the total iron. It seems unlikely that at this pH the difference between the total and ferrous iron can be entirely ascribed to the dipyridyl-stable ferrous complex, since the possibility that formation of the stable complex could be enhanced by an increase in pH is eliminated by the fact that the total-ferrous discrepancy increases so considerably with time.

It seems definite, therefore, that although oxidation proceeds more readily at the higher pH, the oxidation products are stabilized by the formation of a soluble ferric complex which does not, apparently, exist at pH 4.

Variation of the solubilities of iron and aluminium with pH. In order to determine how far the pine extract can influence the solubility of iron and aluminium at high pH values, the following experiment was carried out. A 10 per cent. pine-needle extract was prepared and divided into two equal portions. These were treated respectively with measured excesses of aluminium sulphate and ferric ammonium sulphate. After

being allowed to stand 48 hours to complete the reduction and complex-forming reactions, aliquots of the mixtures were treated with calcium hydroxide solution to give predetermined pH values. The mixtures were then centrifuged and after destruction of organic matter, the amounts of iron and aluminium remaining in solution were determined in the usual manner. The results are given in Table 2, from which it

TABLE 2

		mg./l. retained in solution 10% pine extract	
	pH	*Fe*	*Al*
Iron	4·10	895	..
	6·00	691	..
	8·00	506	..
Aluminium	3·94	..	674
	6·00	..	16
	8·10	..	40

can be seen that very large concentrations of iron are retained in solution, even at pH 8. Since ferrous hydroxide is precipitated in the region of pH 5·5 (Britton, 1942) it is evident that the ferrous iron is present in complex form. In the case of the aluminium, the position is much less definite. Assuming the value of 10^{-32} for the solubility product of aluminium hydroxide (Britton) the experimental figures may be shown to correspond to a rather higher solubility than would be expected in a purely ionic system, from which aluminium would be precipitated at pH 4·1. On the other hand, it can be seen that the results also agree with the observations of Magistad (1925), who found that solution of alumina in sodium hydroxide first becomes perceptible at pH 7·55. Magistad found that at pH 7·55 the solubility amounted to 2 p.p.m., and that at pH 8·35 the value was 8·4 p.p.m.; it seems, therefore, that the pine extract has some influence in protecting aluminium from precipitation, but that the effect is comparatively slight.

Discussion

Since the solution of ferric and aluminium oxides has been found to proceed in the presence of toluene or chloroform, it is reasonably certain that the process is non-microbiological. The shape of the solution curve points to the same conclusion. While the same arguments apply with equal force to the reduction of soluble ferric iron, the initial speed of this reaction is so great as to preclude any possibility of a microbiological mechanism.

The solution and reduction processes have been shown to function under conditions at once neutral and strongly aerobic—conditions much less favourable than are likely to obtain in a podzolized soil. Although the solution effect is considerably smaller under these conditions, it is still appreciable, and is in fact sufficiently great to suggest that under natural conditions this must be an important factor in the translocation of iron and aluminium. It must be noted, however, that since the active

constituents of the pine needles are so readily removed by water extraction, the effectiveness of the fallen needles in any one year would in all probability be exhausted in a comparatively short time under natural forest conditions, although this would naturally take longer for unground needles than for the powdered material used here. Whether decomposition of the needles involves the formation of a further supply of active agents, it is not as yet possible to say.

The relative stability of the ferrous and aluminium compounds at high pH values indicates that reprecipitation of the oxides cannot be caused by the comparatively small changes in pH and degree of aeration which are likely to occur in the soil. An alternative mechanism must therefore be sought in order to explain the formation of the B horizon. Since the iron, and probably the aluminium, can move in the form of metal-organic complexes, assimilation of the organic ligands by microbial action could presumably be the cause of the reprecipitation, although it would be difficult on this basis to explain the segregation of the organic matter, iron, and aluminium in the formation of the B horizon of a well-developed podzol, as well as the consistent order in which these appear.

The rapid initial reduction of soluble ferric iron by the pine extract at first sight suggests that a very powerful reducing agent is responsible. If this were the case, one would expect that the reducing capacity of the extract would fall off very rapidly on exposure to the atmosphere; since, however, the extracts are so stable to atmospheric oxidation, it is suggested that a readily reducible ferric organic complex is first formed, reduction of which is effected by the relatively weak reducers present in the extract. In this case, it seems probable that the formation of the ferric complex is the rate-determining stage of the process.

In conclusion, it may be remarked that the results of this investigation suggest that the process of podzolization appears to show a strong resemblance in detail to that of gleying, as visualized in the light of previous laboratory experiments (Bloomfield).

Summary

1. An aqueous extract of pine needles is capable of causing the non-biological solution of ferric and aluminium oxides; during the solution the ferric iron is reduced to the ferrous state.

2. Solution and reduction take place under neutral and aerobic conditions.

3. The ferrous iron formed by the extract, and possibly the dissolved aluminium, are present in the form of organic complexes.

4. The rate of oxidation of the ferrous complex is low, although it increases appreciably with increasing pH. At pH 7 oxidation appears to result in the formation of a soluble ferric complex, and the total iron in solution remains virtually constant; at pH 4 oxidation results in precipitation of the oxidation products.

5. The ferrous complex is not readily decomposed under alkaline conditions, relatively large amounts of iron remaining in solution at pH 8.

Acknowledgements

The author wishes to acknowledge his indebtedness to Drs. A. Muir and D. A. Osmond for much helpful discussion.

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A STUDY OF PODZOLIZATION

PART II. THE MOBILIZATION OF IRON AND ALUMINIUM BY THE LEAVES AND BARK OF AGATHIS AUSTRALIS (KAURI)

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THE Kauri pine is found only in a limited area of New Zealand, being confined to the northern part of North Island. The tree casts off its bark regularly in large flakes which accumulate around the trunk to form a cone-shaped mound of extremely acid litter. The kauri produces a well-marked A_2 horizon of white silica, which is known locally as 'sugar sand', and in areas in which the kauri no longer grows the presence of this sugar sand has been used by gum prospectors, when seeking the fossil gum, as a means of recognizing the site of former kauri trees (Leeper, 1948). In the strongly weathered soils of N. Auckland the influence of individual kauri trees can be seen in the 'egg-cup' conformation of horizons below them (Crompton, 1951).

The great activity of the kauri as a podzol-former suggested that an investigation of the properties of its debris might provide useful information on the general mechanism of the process.

Materials

The following materials were used in this study:

1. Leaves from a well-established tree, first branch 60 ft. Fairly fresh leaves from fine branches brought down by recent wind. Parua survey district, Whangarei County.
2. Bark from the same tree.
3. Leaves from a yôung tree, first branch 10 ft. Mangakahia survey district, Whangarei County.

The dried leaves and bark were prepared for use by grinding in a Raymond mill.

Experimental

In view of the results obtained previously with Scots pine needles, attention was concentrated on the properties of aqueous extracts of the kauri leaves and bark.

The aqueous extract of the bark is coloured a very intense red-brown, and on standing the solution deposits a dull brown powdery precipitate, consisting, presumably, of tannins. The leaf extracts are much less intensely coloured, but these also give a slight precipitate on prolonged standing. This behaviour introduces an element of uncertainty into the results obtained in experiments extending over several weeks; however, it seems safe to assume that any effect the precipitation would have on the results would be to decrease the amounts of iron and aluminium in solution. Assuming that such precipitation of organic matter does not

occur at the limiting dilution obtaining in the soil solution, it is possible that the effectiveness of the extracts is somewhat greater than appears from the laboratory results.

pH of aqueous extracts. Five-gramme portions of the air-dry materials were shaken for 4–5 hours with distilled water and allowed to stand overnight. After filtering, the extracts were made up to 200 ml. and the pH values determined. The following values were obtained:

	pH
Young leaves . . .	4·2
Old leaves . . .	5·0
Bark	4·6

As in the case of Scots pine needles, steam distillation of the extracts gave no separation of volatile acids. Electrometric titration with alkali gave indefinite results.

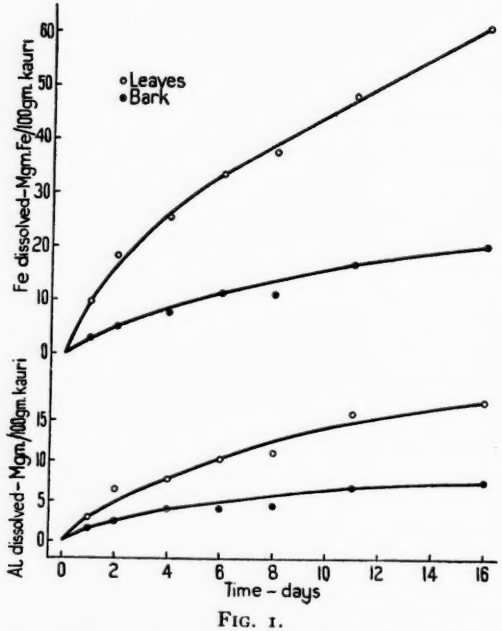

FIG. 1.

Solution of ferric and aluminium oxides. Co-precipitated hydrated aluminium and ferric oxides were treated with 5 per cent. aqueous extracts of the bark and the young leaves. The reaction mixtures, contained in partly filled reagent bottles, were treated with toluene and maintained at 27° C. in the dark with occasional shaking. The dissolved iron and aluminium were determined periodically as described previously. The results are illustrated in Fig. 1, from which it can be seen that the leaves are much more effective in dissolving both iron and aluminium than is the bark.

Comparison of these figures with the corresponding figures for Scots pine needles shows that the latter are less active than kauri leaves, but considerably more active than the bark. Since the pine needles gave a more acid extract than either of the kauri samples, it is clear that the dissolving action cannot be ascribed to a simple acid solution effect.

As in the case of the pine needles, the kauri/iron solutions were found to contain ferrous iron, both the bark and the leaf extracts giving strong qualitative reactions with $\alpha\alpha'$-dipyridyl. Addition of the ammonium acetate buffer to the leaf extract caused coagulation of organic matter; the bulky flocculent precipitate so formed was coloured an intense red by adsorption of ferrous dipyridyl, and consequently it was not possible to obtain a quantitative measure of the amount of ferrous iron present in the reaction solution. This difficulty did not arise with the bark extract, and the following results were obtained after 16 days' contact with ferric-aluminium oxide:

Total dissolved iron . .	0·20 mg. per g. bark
Ferrous iron . . .	0·07 mg. ,,

In neither case was it possible to obtain more than a very approximate estimate of the residual reducing capacity of extracts since coagulation of organic matter took place in both cases on the addition of a ferric salt. However, after removal of the coagulated material by filtration, it was found that the filtrates contained considerably more ferrous iron than the amount of ferric oxide dissolved originally. It is probable, therefore, that as in the case of the Scots pine extract, the kauri material gives rise to a ferrous complex which is too stable to react completely with $\alpha\alpha'$-dipyridyl.

Effect of pH and aeration on the solution of ferric and aluminium oxides. Co-precipitated ferric and aluminium oxides were treated with aqueous extracts of the two leaf samples and of the bark in atmospheres of air and nitrogen. A duplicate series was investigated in which the extracts were previously adjusted to approximately pH 7 by the addition of sodium hydroxide, the apparatus and experimental details being the same as in the Scots pine experiment.

It can be seen from Fig. 2 that the kauri material behaves similarly to Scots pine, although the kauri leaves exhibit a much greater activity than the pine needles. Apart from its smaller activity, the bark behaved similarly to the leaves, and for this reason only one curve relating to the bark is included in the figure.

The two leaf samples gave essentially identical results.

Reoxidation of ferrous-kauri solutions. The ferrous-kauri solutions were prepared in the same way as the ferrous-pine solutions described previously. 100-ml. portions of 10 per cent. bark and young leaf extracts were treated with 100 ml. of N/50 ferric ammonium sulphate solution and left in the dark. Addition of the ferric solution caused the formation of bulky precipitates, particularly in the case of the leaf extract. Initially the precipitate was of a bright purple colour, but after some 24 hours the colour faded to dull buff. The purple colour was presumably caused by

adsorption of a ferric compound on the surface of flocculated organic material, and the disappearance of this colour would result from the reduction of the ferric compound.

After having been left for 2 days, each of the mixtures was divided into two equal portions and these were treated with sodium hydroxide

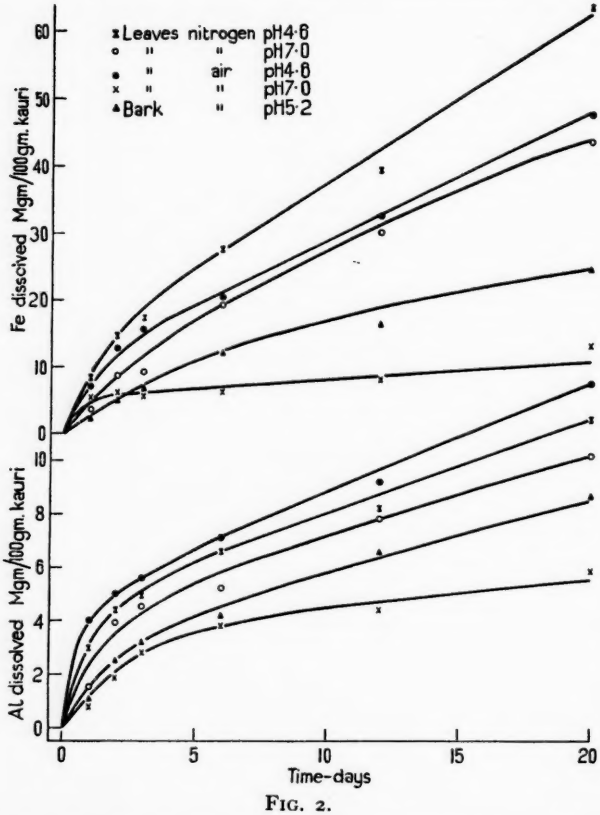

FIG. 2.

solution to give pH values in the region of 4 and 7 respectively. Addition of the alkali appeared to cause partial re-solution of the flocculated organic material. The mixtures were then centrifuged and the clear liquids treated with toluene and shaken in partly filled bottles, the total and ferrous iron remaining in solution being determined at intervals. The results are shown in Fig. 3, from which it can be seen that in comparison with the bark extract the leaf extract is much less affected by raising the pH. In all cases the total and ferrous iron curves are approximately parallel, so that oxidation of the kauri-ferrous compounds apparently results in precipitation of the oxidation products, and not in the formation of a soluble ferric complex as seems to be the case with

Scots pine at the higher pH. The kauri bark extract is clearly not capable of preventing the precipitation of the greater part of the iron when the pH is increased.

Variation of the solubilities of iron and aluminium with pH. In this experiment 10 per cent. extracts of the young leaves and of the bark

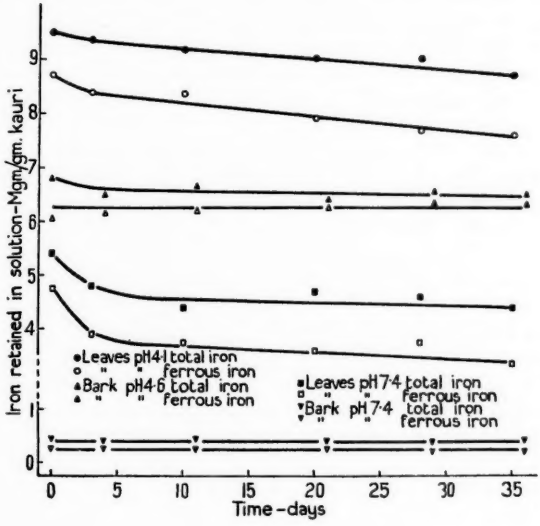

FIG. 3.

were treated with excess ferric ammonium sulphate and aluminium sulphate solutions as described in the previous paper. As before, a saturated solution of calcium hydroxide was used to adjust the pH of the mixtures. While the addition of calcium ions had no apparent effect on the Scots pine extract, it was found that both the kauri leaf and bark extracts gave bulky precipitates when so treated. In view of the ability of this precipitated material to adsorb ferrous iron, it is probable that the results given in the table are proportionately lower than would be obtained at limiting dilutions.

	Leaves		*Bark*	
	pH	*mg./l. retained in solution. 10% kauri extract*	*pH*	*mg./l. retained in solution. 10% kauri extract*
Iron	3·92	1,450	4·14	870
	5·96	1,140	6·16	320
	7·84	380	7·90	3
Aluminium	4·00	640	3·90	730
	6·04	8	6·06	1
	8·14	19	8·10	38

Discussion

As has been mentioned earlier, the kauri extracts contain comparatively large amounts of readily flocculated organic material, the presence of which prevents as complete an investigation of the properties of the extracts as was possible in the case of Scots pine. Nevertheless, the essential similarity between the effects produced by the litter of the two trees is reasonably well established.

In view of the production of ferrous compounds by the kauri litter, even under aerobic conditions, it is clear that, as in the case of gleying (Bloomfield, 1951), the mobilization of iron in podzol formation involves both solution and reduction of ferric oxide; the question of the relationship between the two processes therefore arises.

The mobilization of ferric oxide could be due to the continuous disequilibrium caused by reduction of the limiting amounts of ferric iron dissolved by water, both solution and reduction thus being produced solely by reducing compounds which need not otherwise have any effect on the solution of the ferric oxide. Alternatively, solution of ferric oxide may be directly promoted by a complexing agent, quite independently of the subsequent reduction. It is possible, of course, that in the second alternative both functions could be filled by one molecular species, the organic ligand being autoxidized at the expense of the ferric ion.

If the process were caused solely by reducing compounds, it would be expected that certain broadleaved trees, e.g. oak, would be capable of causing podzol formation by virtue of the tannins present in their leaves. By the same reasoning, the kauri bark should presumably be more active than the leaves or, for that matter, Scots pine needles. (Determination of the tannin contents of kauri bark and pine needles, by the hide powder method, gave values of 8 and 2 per cent. respectively.) Since the evidence does not agree with these suppositions, it seems most probable that, in addition to reducing substances, both Scots pine and kauri produce substances which promote solution of ferric oxide, and as the reaction takes place at pH 7 and above, there can be little doubt that the solution takes place by virtue of complex formation.

When one considers that podzol formation is associated with coniferous as opposed to broadleaved trees, and that a characteristic of the former is the secretion of gums and resins, it seems possible that it is the presence of resin acids in the conifers which confers on them their podzolizing properties.

It has been shown that the pine-needle and kauri-leaf extracts give rise to very stable ferrous complexes, while the kauri bark is considerably less effective in this respect. Since the resin content of the bark would be expected to be considerably smaller than those of the pine needles and kauri leaves, perhaps the formation of the stable complex too can be ascribed to the water-soluble constituents of the pine and kauri oleoresins. In this connexion it may be mentioned that it has been found that while fermenting oak leaves will dissolve and reduce appreciable quantities of ferric oxide under anaerobic conditions, the ferrous compounds formed undergo oxidation and consequent precipitation within a few minutes of their exposure to the atmosphere.

Summary

1. Both the leaves and the bark of the kauri contain readily extractable water-soluble compounds which will dissolve ferric and aluminium oxides, the former being reduced to the ferrous state, even under aerobic conditions.

2. The ferric oxide is mobilized in the form of a ferrous organic complex of considerable stability.

3. The action of the kauri litter resembles that of Scots pine to a marked degree.

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STUDIES IN PEDOGENESIS IN NEW SOUTH WALES

IV. THE IRONSTONE SOILS

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SOILS containing massive or pisolitic ironstone are of common occurrence in Australia, and in recent years most of these have been described as 'laterites' (Prescott, 1932; Whitehouse, 1940; Voisey, 1945; Stephens, 1946), the presence of the ironstone horizon alone being accepted as an adequate criterion of the 'laterite' profile.

Observations in New South Wales suggest that the soils containing a massive ironstone horizon require to be subdivided into two broad groups which may be described tentatively as those showing a 'laterite' profile and those showing an 'ortstein' profile, and the points of difference and similarity illustrated by reference to certain profiles seen by the authors.

The 'Laterite' Profiles

There has been considerable revision in the last few years as to what constitutes laterite, and Pendleton (1939, 1942, 1947) in particular has drawn attention to the variation in chemical and mineralogical composition of the indurated horizon. Much less has been written on the associated or companion horizons, and since this formation has been found to occur in New South Wales in a wide variety of rocks scattered across the State, a description of the variations encountered is necessary to an understanding of the soil formations of the present day.

The profiles examined may be divided into three sub-groups depending on the composition of the indurated horizon, namely, the ferruginous, bauxitic, and manganiferous laterites, and further subdivided into profile variants by the presence or absence of a silicified zone, the telescoping of the profile, and the occurrence of two or more laterite profiles superimposed in the solum (Table 1).

TABLE 1

Classification of the Forms of Laterite observed in New South Wales

Simple laterites	*Multiple laterites*
Ferruginous laterite	Ferruginous laterite
Ferro-mottled laterite	Ferro-mottled laterite
Bauxitic laterite	Bauxitic laterite
Manganiferous laterite	..
Mangano-mottled laterite	..
Mangano-pallid laterite	..
Silicified ferruginous laterite	Silicified ferruginous laterite
Silicified ferro-mottled laterite	Silicified ferro-mottled laterite
Silicified bauxitic laterite	..

Present Environment of the Laterites, and their Role as a Parent Material

In New South Wales laterites appear to be generally fossil soils and are found under a wide range of climates.

Their occurrence bears no relationship to the present physiography. They may be found as cappings on isolated hills, at the bottom of valleys and basins, at all positions on the slopes, and are in no way related to present water-table conditions.

They occur on a variety of rocks, from acidic to very basic, and although the profiles maintain the same essential features, some of the variations in them appear to be associated with differences in parent material.

Although locally laterites may be characterized by particular types of vegetation, in general there is a complete lack of correlation, and they have been observed under plant communities as diverse as desert grassland and wet sclerophyll forest.

It is thus apparent that the present-day spatial relationships of laterites with other soil groups cannot be interpreted pedogenically.

The laterites in N.S.W., therefore, are to be regarded as parent materials for the formation of soils under post-lateritic conditions of climate, physiography, and vegetation cover.

In the simplest cases, pedogenesis has occurred within the original laterite profile which has remained virtually untruncated. Depending on past and present conditions, a wide range of soils has now developed in the laterite profiles throughout the State, including representatives of groups as diverse as podzols, chernozems, and solonchaks. Consequently, laterite profiles, even within the same area, may now differ widely in many of the properties which have since been superimposed upon them, such as degree of podzolization or calcification, pH, and organic carbon content. This is evident from some of the following profile descriptions particularly those in which the occurrence of secondary calcium carbonate or gypsum has been recorded.

Where the post-laterite environment, as regards climate or physiography, has been less favourable for the preservation of the laterite profile against erosion, varying degrees of profile truncation have occurred. The soils now developed on the truncated laterites may vary considerably depending on the particular horizons which have been exposed. The soil pattern in such areas has been complicated further by the super-position of subsequent pedogenic processes, as described above for the untruncated profiles.

The lateritic materials derived by the truncation of the original profiles are frequently found redistributed as secondary soil materials in lower situations. These materials have also been modified in the course of subsequent pedogenesis to form present-day soils.

Description of certain Laterite Profiles

Ferruginous laterites

Much of the Sydney district is covered by the horizontally bedded sedimentary rocks of Triassic age. Many exposures are seen of laterite

developed on Wianamatta shale, and a few cases where it appears to have formed on Hawkesbury sandstone. In many cases where the overlying Wianamatta shale is fairly shallow, the laterite extends through both rocks, giving a profile rather different from that developed on either. This effect does not appear to have been recognized elsewhere.

The Sutherland Profile. A profile developed on Wianamatta shales, across the crest of a low hill, is exposed at Sutherland Brick Works. At the west side of the pit the profile is

0″	Orange-brown gravelly loam; numerous ironstone pebbles; fine crumb, moderately friable; merging gradually into
8″	Grey-brown gravelly loam; pisolitic ironstone gravel as above; cloddy to massive; firm; merging gradually into
1′ 4″	Orange clay; massive; compact; merging into lower layer.
2′ 6″	Orange clay, becoming mottled with white as depth increases; merging into
15′	White clay; but preserving the laminated structure of the shale towards the base. Sharply defined but irregular junction with
30′	Dark grey shale.

Lumps of massive ironstone (Plate VIII) occur 100 yds. from the edge of the pit, under relatively undisturbed sclerophyll forest. A freshly fractured surface shows a reticulate mottling of purple with streaks of orange-brown and separate yellow fleckings. The purple material is hard, and the orange-brown material is softer and more earthy.

The Wattamolla Profile. A profile developed on Hawkesbury sandstone is exposed by erosion in an old gravel pit above Wattamolla Beach, National Park.

The profile is

0″	Yellow-brown gravelly loamy sand; almost single grain structure; loose. The gravel is angular, covered with a thin brown patina of iron oxide, and on fracture has the appearance of ferruginous sandstone. This merges into
4″	Grey-brown loamy sand; gravel as above but increasing in size until it forms the massive indurated horizon below (Plate I*a*). (The indurated material may be exposed at the surface.)
1′	Dark brown massive indurated zone. On fracture appears like porous ferruginous sandstone at the top (Plate IX), becoming vermicular at the bottom, the tubules being filled with an orange-brown earthy material. Sharp change into
2′	Brown-orange sandy clay; massive and compact; with red flecks at the top and white fleckings increasing downwards to
5′	White sandy clay; friable yet compact; containing some grains of quartz up to $\frac{1}{8}$ in. long. Becomes sandier and more friable with depth, although still completely bleached. Changing sharply into
8′	White clayey sand to white soft sandstone, with large sharply defined patches of purple material of similar character. At lower depths are massive blocks of slightly altered sandstone.

The pallid zone cuts at an angle through the current bedding of the sandstone (Plate I*a*). On slightly higher ground south of this site the indurated and mottled zones have been removed and a thin grey soil overlies the massive Hawkesbury sandstone, the upper portion of which is generally white and often soft, and probably represents the exposed pallid zone.

The French Profile. A deep profile developing through both Wianamatta shale and Hawkesbury sandstone is exposed in gravel pits at the

trigonometric station at French, 9 miles north of Sydney. The full profile can be described by considering the pits on both east and west of the road (Plate II*a* and *b*).

0″ Dark brown indurated zone, thickly studded with iron pisolites (Plate XII), giving way abruptly to

1′ 6″ Yellow-brown clay; compact though moderately friable; pisolitic gravel similar to that above is plentiful but diminishes and disappears at depth. The clay hardens on exposure to air. Merging into

8′ Yellow-brown clay; structure and consistency as above; with red, purple, and white mottlings, which grow larger and are dominated by white at depth. Merging into

21′ White sandy clay, lightening in texture to clayey sand. This changes sharply into

25′ Decomposing sandstone, showing white and purple angular colorations similar to Wattamolla. The colours are patchy and sharply defined.

Considerable variations are shown in the indurated zone of profiles developed in the Sydney district, some of which are illustrated by Plates VIII–XII. In many parts the indurated zone has been entirely decomposed, but its former presence can be recognized by the pisolitic ironstone gravel lying on the surface or accumulating on ant-hills.

The Newell-Pilliga Profile. A profile of a silicified ferruginous laterite developed on Jurassic shales in the Pilliga scrub has been exposed by a road cutting on the Newell Highway (Plate III*a*).

0″ Red-brown sandy soil, single grain to weak crumb; incoherent; containing many large honeycomb pisolites up to 1 ft. (Plate XIV). Quartz pebbles and iron oxide coated sandstone floaters sometimes present. Sharply defined from

1′ 3″–1′ 8″ Dark brown indurated ironstone, sometimes slightly vesicular. Sharply defined from

1′ 8″–2′ Purple-brown, laminated indurated horizon; laminae ⅛ in. thick; mottled with concentric red and yellow iron oxide (Plate XIII). Sharply defined from

2′ 4″–3′ Mottled white and red clay; compact; extending in long tongues into

3′ 4″–4′ White kaolinitic clay, maintaining structure of original shale. Generally soft, but in parts hard due to thin coat of silica along cleavage lines of shale. Sharply defined from

5′ 4″–7′ Decomposing shale.

The Jindabyne Profile. A ferro-mottled laterite is developed on granitic colluvium in a broad ancient valley, 5 miles east of Jindabyne on the Berridale road.

0″ Ashy-grey gravelly loam; poor crumb; friable; containing ironstone and quartz gravel; locally indurated where massive ironstone still persists. Well defined from

1′ 8″ Yellow/red mottled gravelly clay loam; prismatic; compact; gravel as above; blue-black stains of manganese in cracks. Merging gradually into

3′ 9″ Bright orange-yellow gravelly clay loam; quartz and rock gravel abundant. Fossil worm tracks impregnated with iron and manganese oxides. Merging into

4′ 9″ Granitic colluvium.

The Wolfram Hill Profile. A multiple ferruginous laterite profile developed on granitic colluvium on the lower slopes of a broad valley is exposed in an erosion gully on Wolfram Hill, west of Berridale (Plate III*b*).

0″ Light grey gravelly sandy loam; weak crumb; loose; gravel consists of nodules and fragments of massive ironstone.

1′ 11″ Dull brownish-red massive concretionary ironstone, with individual pisolites up to 1 in. in diameter. Sharply defined from
3′ Orange/white mottled clay loam; prismatic to semi-columnar with purplish-black manganiferous stains along cracks. Amorphous calcium carbonate present in small amounts. Merging into
5′ 6″ Pale orange/white mottled clay becoming paler with depth and lacking purple stains; weakly prismatic. Calcium carbonate as above. Fossil worm (?) holes present, impregnated with iron. Merging into
7′ Almost white clay, occ. stained yellow. Calcium carbonate as above. Resting abruptly on
9′ 2″ Dark brown massive concretionary ironstone (as above).
10′ 2″ Orange/white mottled clay as above, gradually changing through pale orange/white mottled clay as above, and merging into
15′ Almost white clay. This passes into
17′ 2″ Weathered transported material.

Bauxitic laterites

The Tingha Profile. A silicified bauxitic laterite developed on sedimentary rocks between Tingha and Stannifer has been exposed (Plate IV*a*) by an open-cut tin-mine at the foot of a low hill capped by the indurated horizon, which prospecting trenches show to have a depth of some 50 feet.

The profile is

0″ Red gravelly loam; fine crumb; very friable; containing small concretions of sesquioxides most of which crush fairly readily. Changing fairly sharply into
8″ Red gravelly loam; fine crumb; friable; concretions as above; merging gradually and unevenly into
1′ 6″–2′ Red/purple mottled clay; semi-columnar; compact; white mottlings begin about 2 ft. 6 in. and increase with depth.
14′ White friable clay; capped in part by a silicified zone about 12 in. thick (Plate IV*b*) and seamed through with thin veins of silica at irregular intervals.

The silicified material is analogous to that described as 'Grey Billy' in western New South Wales (and Queensland) and is pure quartz.[1]

The soil at the base of the hill, at the eastern end of the exposure, is completely lacking in red coloration, nor does the profile contain any mottled horizon but is yellow-brown to grey-brown in colour and much coarser in texture. This is similar to the material that overlaid the tin-bearing gravels, in the exploitation of which the excavation was made. It is noteworthy that the stanniferous concentrates no longer appear where the complete laterite profile is encountered, though they were at this site largely if not entirely underlain by the pallid zone. This would imply that the tin-bearing gravels were laid down some time after erosion of a well-developed laterite.

The Emmaville Profile. A comparable profile to the one just described has been exposed, again by open-cut tin-mining, just west of Emmaville. The exposure shows a bauxitic indurated zone of 6 to 10 ft. (Plate V*a*), beneath which lies a narrow and poorly developed mottled zone, underlain in turn by a pallid kaolinized zone of more than 5 ft. Some silicification of the kaolinized material of the pallid zone has taken place, forming a pavement in parts of the excavation.

[1] Analyses by M. Woof.

The Fernhill Profile.[1] A profile of a bauxitic laterite on basalt is exposed in a quarry at Fernhill, Inverell (Plate V*b*). It occurs near the top of a hill of basalt, the whole crest of the hill being covered by a 'snuffy' red soil containing lateritic pisolites and underlain by a massive indurated horizon. The profile is as follows:

0″ Bright red loam; fine crumb; friable; containing irregular concretions, mostly hard but some of which crush readily. Merging into
1′ Bright red clay loam; with more frequent concretions
4′ Red indurated zone, of large nodular concretions of irregular shape, largely composed of goethite and haematite, in a reddish clay matrix (Plate XVI). Changing quickly into
9′ Orange to red clay, containing spherical to irregular hard nodules of bauxite. Sharply defined from
12′ 9″ Red and white mottled clay with white mottlings increasing downwards. Resting abruptly on
16′ 3″ Light brown to olive-green kaolinitic clay, with small white mottlings associated with vermicular holes. Little change visible at deeper levels (quarry extends to 23 ft.).

The Bunyan Profile. A multiple bauxitic laterite developed in basaltic colluvium in a broad ancient valley is exposed 1 mile west of Rock Flat Creek on the Bunyan–Rose Valley road.

0″ Dull brick-red indurated zone, of large sub-spherical concretions of bauxite, containing small pisolites; some amorphous gypsum. Merging into
1′ Bluish-red mottled heavy clay; gypsum as above; merging into
2′ Bluish-white heavy clay, stained orange near lower laterite profile. Large gypsum crystals abundant. Sharply defined from
3′ Bright red heavy clay. Gypsum as above. Merging into
3′ 9″ Orange/yellow mottled heavy clay, becoming bluish-white below. Gypsum as above. Merging into
4′ 3″ Greyish-white heavy clay, becoming paler with depth. Large gypsum crystals fairly common.

Manganiferous laterites

The Berridale Profile. A simple mangano-mottled laterite developed on granite on the gentle slopes of a broad valley is exposed 1 mile south-east of Berridale on the Berridale–Bobundara road.

0″ Ashy-grey gravelly loam, locally stained black from decomposing nodules of manganese oxide, merging into
11″ Dark reddish-black massive indurated horizon. Mainly concretionary manganese oxide, with some iron oxide. Sharply defined from
1′ 9″ Yellow-grey mottled gritty clay, with some manganiferous gravel in the upper portion. Merging with
2′ 9″ Decomposing granite.

The Bobundara Profile. A simple mangano-pallid laterite developed on granite is exposed near the base of a gentle slope 1 mile west of Wullwye Creek on the Berridale–Bobundara road (Plate VI*a*).

0″ Black to reddish-black massive concretionary manganese oxide, with some iron oxide. Individual concretions up to 2 in. in diameter. Quartz gravel fairly abundant. Abruptly demarcated from
3′ White gravelly clay loam. Quartz gravel fairly abundant. Merging into
8′ Decomposing granite.

[1] This profile has been subject to detailed chemical and mineralogical analysis by D. Carroll and M. Woof (1951, Soil Science, **72**, 87).

Although ferruginous laterites containing manganese have been described previously (Joffe, 1936; Bryan, 1938; Teakle, 1950) the manganiferous laterite, with a massive indurated horizon of manganese oxide, does not appear to have been recorded. In the authors' experience these are limited in New South Wales to the Monaro Region, where many separate exposures have been seen.

The poly-indurated lateritized gravels

A number of profiles have been seen in different parts of the State which appear to be variants of the multiple ferruginous laterites. They differ from others previously described in the presence of a greatly increased number of indurated horizons, which are usually very thin.

The Dubbo Profiles. A sequence of these profiles occurs in a gravel pit at Dubbo.

The pit exposes a series of beds of pebbles ranging in size up to 2 in. across, obviously of fluvial origin, and rounded in shape. Through these gravels are layers cemented together by a ferruginous deposit, generalized throughout the band but forming at different levels thin distinct layers, the thinnest to form a coherent induration being only $\frac{1}{10}$ in. thick. The bands are usually roughly parallel to each other. The finer material deposited between the pebbles has been consolidated almost to the consistency of rock. These multiple indurations cover a depth of about 4–5 ft.

Below this, the gravel beds have a bleached appearance, even between ferruginous layers only 1 in. to $1\frac{1}{2}$ in. apart. Up to 20 of these thin indurated bands are present, one above the other.

The St. Mary's Profile. The extensive Tertiary deposits lying east of the Hawkesbury river, about 20 miles west of Sydney, appear to have been largely if not entirely lateritized. Numerous exposures similar to the one described below can be seen in road cuttings and in the excavations for the Warragamba pipe-line.

A profile in gravel beds is exposed in the cutting at St. Mary's railway station (Plate VI*b*). North of the line the profile shows:

0″	Brown gravelly loam, containing much ironstone gravel $\frac{1}{8}$–$\frac{1}{4}$ in. diameter, which commonly accumulates on the surface. Texture changes gradually to brown gravelly clay.
1′–3′	Mottled orange, yellow, and purple clay, soft when moist but hardening on exposure to rock-like consistency, standing out as an overhanging edge. Merging into
6′–9′	White friable clay, seamed with numerous layers of indurated iron oxide which are grouped in bands, separated by zones of kaolin. They are not a constant distance apart, but merge towards the edge of the cutting. The large white stones are of yellow sandstone, covered by a thin skin, less than $\frac{1}{16}$″ thick which has been completely leached of iron. Merging into
20′	Decomposing alluvium.

Ironstone in the desert soil formations

Ironstone pisolites are a common feature in both of the two main desert soil formations.

In the Seif Dune soils the inter-dune corridors are commonly sprinkled with uniformly graded pisolites, which have probably been carried by

stream flow from the Stony Downs soils of the higher areas (Hallsworth, Gibbons, and Darley, 1951).

The Stony Downs soils themselves carry a relatively heavy stone layer in the surface, consisting of varying proportions of small ironstone pisolites, pebbles of opaline quartz, and stones of secondary quartzite (Grey Billy) which range up to quite large boulders.

These two soil groups will form the subject of a subsequent paper, but the presence of both the ironstone and the 'Grey Billy' can be explained on the hypothesis of Whitehouse (1940) that Stony Downs are largely residuals from former laterites whilst the Seif Dune soils are derived from the redistributed material that has been eroded from them.

The large proportion of 'Grey Billy' in the stony layer suggests that the original laterites of this area were largely silicified.

In the profiles described here, silicification is very variable. It is completely lacking in most, whilst in the Newell-Pilliga profile and the Emmaville profile parts only of the pallid zone have been silicified, the silicification occurring as a skin around blocks of kaolinized material. In the Tinga profile, however, the silicified layer extends as a coherent sheet over considerable areas. This type of silicification on an even more extensive scale has been described for western Queensland by Whitehouse (1940) and in western New South Wales by Kenny (1934), although a complete laterite profile showing the heavily silicified layer has not yet been described in New South Wales.

Inspection of these profiles suggests that silicification has taken place after the general development of the other features, and that the silicified horizon is not a normal or invariable horizon of the laterite profile.

Pedogenesis

General

Although the occurrence of laterites in New South Wales is independent of present environmental conditions, and it is clearly impossible to develop a completely adequate theory of the chemical processes involved in their formation from fossil profiles only, an examination of their profile morphology, both with regard to those features which are invariably present and to those which vary, allows certain conclusions to be drawn.

Nearly all the profiles described above show a characteristic pattern of three horizons:

(i) An horizon which may be pisolitic, laminated, or massive, and which consists largely of the oxides and hydroxides of iron, aluminium, or manganese.

(ii) Below this lies the mottled zone of yellows, orange, reds, and purples and sometimes blacks with white fleckings. These fleckings increase in proportion towards the bottom of the zone, and ultimately in most cases give way to

(iii) The pallid zone, of white or creamy material, in which the clay is entirely kaolinite, although varying and sometimes large proportions of quartz grains are present. In certain cases part of this layer may be silicified.

Below the pallid zone is decomposing rock, giving way ultimately to the unweathered rock beneath.

This characteristic pattern appears to be the result of the concentration of the sesquioxides in one zone, whilst at the same time they have been almost entirely removed from a lower zone of variable but commonly very considerable dimensions.

The conditions under which such marked migration and accumulation of sesquioxides could take place may be analysed further.

Iron and manganese would become mobile under conditions which were either strongly acid or strongly reducing, and the further possibility exists that either of these metals could become mobile through the formation of complexes with organic acids or other compounds from the humus (Bremner *et al.*, 1946).

Aluminium, on the other hand, shows increased mobility only under the influence of increasing acidity and is not affected by variations in the redox potential of the system, nor on the basis of present evidence, by the formation of complex metallo-organic compounds.

The conditions under which precipitation of these ions from solution takes place also imply some degree of differentiation.

Aluminium, on the one hand, may undergo precipitation as kaolinite either by combination with silica (colloidal or in solution), or may be precipitated as one of the forms of hydrated aluminium oxide simply with change in pH or by dehydration of the suspension. The formation of clays of the montmorillonite-beidellite group appears to be unlikely under the strongly acid conditions that would permit mobilization of the aluminium.

Iron and manganese, on the other hand, may be precipitated as hydrated oxides or hydroxides by change in the pH, by concentration beyond saturation point due to removal of water by evaporation or transpiration, or by oxidation at the air–liquid interface, or by bacterial action.

The pallid zone represents an horizon of sesquioxide depletion. This could develop most readily in a zone of permanent saturation with water, which would impose anaerobic conditions, whereby iron and manganese present in the rock minerals or as sesquioxides would be brought into solution in a reduced condition. If, furthermore, conditions were sufficiently acid, aluminium would also be mobilized.

The presence, in addition, of colloidal or soluble silica would lead to the formation of kaolinite by mutual precipitation of some part with the aluminium. There will be a range of values for the ratio of silicon to aluminium where their precipitation as kaolinite will be most favoured. The solution in such cases would contain less aluminium, with the result that the higher zone of deposition formed would contain proportionately more of the oxides of iron and manganese.

If after precipitation of the aluminium as kaolinite, the soluble silica were still considerably in excess, and its removal by underground drainage restricted, it could be deposited near the base of the profile, with resultant silicification of parts of it.

Under conditions of restricted drainage, the movement of most of the

sesquioxides from the pallid zone would take place mainly in an upward direction. This movement would take place when the water-table and hence the zone of reduction were rising.

The mottled zone corresponds to this zone of periodic water-table fluctuation, in which reducing conditions would follow the rise of the water-table, and oxidizing conditions return when the water-table falls. During periods of high water-table, iron and manganese would be in solution in the reduced condition. Aluminium would also be in solution provided that the ground water was sufficiently acid.

Further upward movement of these solutions by capillarity would take place above the upper level of the water-table. Following the work of Penman (1941), it would not be expected that such capillary movement would normally extend to the surface, although it might do so under particular conditions of humidity.

With the fall of the water-table and reimposition of oxidizing conditions, some of the iron and manganese would be precipitated from solution by oxidation, and iron, manganese, and aluminium by concentration or by decreased acidity.

These processes may be responsible in part for the characteristic mottling of colours of this zone referred to above, the colourings being due to the various oxides and hydroxides of iron, aluminium, and manganese, whilst the white fleckings, increasing towards the pallid zone, are due to kaolinite and to bleached quartz grains.

The depth of the mottled zone will depend upon the extent of the water-table movement from its average lower level during the drier periods to its average upper level during the wetter periods. In special cases where virtually no vertical water-table movement occurs the mottled zone will fail to develop. The uppermost zone of sesquioxide accumulation corresponds to the zone into which solutions are withdrawn by capillarity from the ground waters when the water-table is near its upper level.

As these solutions in moving upwards become progressively more concentrated, dehydrated, and perhaps less acid, oxides and hydroxides would be precipitated, leading to the development in the area of maximum precipitation of a pisolitic, laminated, or massive structure.

Any sesquioxides dissolved from the upper layers by leaching might be deposited directly in the indurated zone, or more probably carried into the ground waters, from which they would be subsequently deposited in the manner described above. Such downward leaching would take place during the wet season.

The mantle of soil overlying the zone of sesquioxide accumulation would be expected to vary according to the parent material. On very coarse textured or siliceous rocks, this soil would exhibit podzolic features, whereas on finer textured rocks, or those richer in ferromagnesian minerals, krasnozem features would be developed.

The processes outlined above would account for the invariable features of the laterite profiles that have been described. It remains to consider in greater detail the factors responsible for the variations encountered.

Climate

A tropical climate characterized by alternate wet and dry seasons is generally considered to be essential for laterite formation. This statement appears capable of some modification. Although the climate must be sufficiently warm to produce deep and intense weathering and alternate wet and dry seasons would most readily induce the necessary fluctuations in the water-table, such seasonal variation in rainfall is not essential. A similar effect could be accomplished by alternate warmer and cooler seasons with more or less constant rainfall. Decreased evaporation and transpiration during the cooler season would allow the water-table to rise, particularly in favourable physiographic situations, whilst increased water loss during the warmer season would lower it again. According to this view laterite formation could also take place under sub-tropical or even warm temperate conditions.

Topography

The generalization has also been made that the water-table fluctuations involved in laterite formation require peneplain topography. This statement also requires some modification, since the laterites of New South Wales, whilst frequently occurring in situations suggestive of peneplain remnants, are also found in basins and along the floors and gentle slopes of broad and ancient valleys. In a few instances, furthermore, laterites appear to have formed even on moderate slopes, but limited in this case to the lower catenary positions.

On peneplain topography the fluctuations in water-table necessary for the development of the laterite profile could only occur with a marked alternation of wet and dry seasons.

On undulating topography, however, laterite formation becomes less dependent on climate. Since the variations in water loss by evaporation and transpiration from the catena as a whole, due to seasonal fluctuations in temperature, are magnified by topographic concentration, considerable fluctuations in the level of the water-table may occur at the base of the catena, even without marked seasonal fluctuations in rainfall. These conditions appear to have been important in certain cases.

It follows as a corollary from the foregoing that the occurrence of laterite residuals is not prima facie evidence of the previous existence either of peneplain topography or of a tropical climate.

Under limiting conditions of climate and parent material, topography, through its effects on the lateral movement of ground-water downslope, appears to have been of particular importance in the transport of sesquioxides from higher slopes and their accumulation in lower situations. In this manner the water-table in these situations may contain a much higher content of sesquioxides than could be derived from rock weathering *in situ*. Topographic concentration of sesquioxides and their subsequent deposition in the upper laterite horizons (Campbell, 1917; Greene, 1947) becomes important in the genesis of laterites on rock materials naturally deficient in iron, aluminium, or manganese, as for example on the acid gneissic granites of the Monaro or on the Hawkesbury sand-

stone around Sydney. The process of topographic concentration of sesquioxides is essentially similar to the process of base concentration in the calcimorphic soils of the present day (e.g. Hallsworth, Costin, *et al.*, 1952).

Permanent changes in the level of the water-table may also be important in the development of laterites. In areas where the base level of erosion has been attained and entrenchment of the watercourses cannot proceed farther, the vertical fluctuations of the water-table during wet and dry seasons (or relatively cool and warm seasons) will recur in the same zones of soil over a long period of time. Such conditions would result in the formation of a zone of sesquioxide accumulation virtually limited to the maximum effective distance of capillary movement for the texture of the particular soil material concerned; but the sesquioxide concentration would be extremely high owing to the length of the time interval during which the same water-table influences were being repeated. The extreme density and hardness of the so-called lateritic duricrust on peneplain residuals of New South Wales supports this view (Wattamolla and French profiles).

In areas where the base level of stream entrenchment has not been attained, however, and where the watercourses are still cutting downwards, the water-table would be lowered gradually and the precipitation of sesquioxides would thus occur at progressively lower levels. At the same time rock weathering would occur at greater depths and fresh mottled and pallid zones would be formed. If the lowering of the water-table proceeded sufficiently slowly there would be virtually no discontinuity in the zone of sesquioxide accumulation which would extend downwards into what hitherto had been mottled and pallid zones. The latter zones, on the other hand, although continuously changing their position in a vertical direction, need not change appreciably in thickness. In this manner the zone of sesquioxide accumulation would develop to a thickness not only far greater than the effective distance of capillary movement but also out of all proportion to the relatively shallow mottled zones below. This condition could have existed, for example, in the formation of many of the laterites of the New England region (cf. Fernhill and Emmaville profiles), and elsewhere in the State.

Relatively sudden, as opposed to gradual entrenchment, would operate with different results. Under these conditions the area of sesquioxide deposition would change suddenly from a higher to a lower level, resulting either in a discontinuity in the sesquioxide horizon or, where the changes in the level of the water-table were greater, in the isolation of all of the original laterite profile and the genesis of a completely new profile below. Additional sudden changes would initiate the formation of still more profiles. This offers an explanation for the origin of the multiple laterites referred to earlier (cf. Bunyan and Wolfram Hill profiles).

Profile replication may have occurred either on a regional or a quite local scale. The former would obtain where the land surface was undergoing uplift, relatively sudden earth movements resulting in correspondingly more rapid stream entrenchment followed by profile replication.

The regular recurrence of such profile replication throughout a region may help in interpreting the geological history. Where the profile replication varies in the same locality, on the other hand, it is to be inferred that the entrenchment of the watercourses has been due to local influences such as the occurrence of relatively hard and soft bands of rock. The retardation of entrenchment by a layer of hard rock would lead to a period of constant water-table level accompanied by lateritization, followed by a period of rapid entrenchment through the softer rock until the next hard layer was encountered.

The individual profiles of the multiple laterites formed locally in this manner would be expected to be shallower than those due to regional earth movements. In extreme cases, as at St. Mary's, near Sydney, and at Dubbo some of the individual profiles are no more than an inch thick. The individual profiles of the multiple laterites in the Monaro Region are commonly 2–5 ft. in thickness, and some of those near Sydney up to 10 ft.

If the level of the water-table were to rise relative to the laterite profile already present, as would be caused by downward earth movements such as slow sinking or faulting or by increased precipitation on a land surface at base level of erosion, the sesquioxides of this initial profile would be removed upwards into a new profile which would begin to form above. The mottled and sesquioxide zones of the original laterite would now become bleached and almost indistinguishable from the underlying pallid zone, with the result that the later profile, when finally formed, would contain an extremely thick pallid zone relative to the higher horizons of the profile. Some of the very deep pallid zones in laterite profiles of the Hawkesbury and Wianamatta series of the Sydney district may be accounted for in this way.

Geology

The composition of the parent rock is frequently the determining factor in the formation of a laterite of a particular subgroup and the mode of occurrence of the sesquioxides themselves.

In all areas of the State where basalt has been the parent material for laterite, bauxitic laterites have developed. These are characterized by the dominance of alumina in the zone of sesquioxide accumulation, together with sufficient ferric oxide usually to impart a bright red colour. Owing to the greater proportion of alumina, the indurated horizon, although still massive in structure, is relatively soft, porous, and light in weight compared with the similar horizons of the ferruginous and manganiferous laterites, the individual pisolites (or nodules) typically occurring as separate units within an earthy groundmass (e.g. Fernhill and Bunyan Profiles). In consequence, the indurated zone of the bauxitic laterites is more readily removed by post-laterite erosion, during which period the bauxitic pisolites break up so completely that they are never found far from their parent profile.

The formation of ferruginous laterites has occurred on almost all other rocks. The zone of sesquioxide accumulation characteristically contains a dense, massive ironstone layer which has been highly resistant to post-laterite weathering and erosion. The massive horizon may consist

of pisolitic ironstone in which the pisolites have been joined together by mutual cementation, or of a dense band of relatively pure ironstone deposited in the form of a continuous sheet. Owing to their extremely dense structure, the ferruginous pisolites resist abrasion and weathering, and may in consequence be transported for considerable distances from the parent laterite (Stephens, 1946).

The manganiferous laterites of the Monaro Region have so far been found only in association with basic granites. It is not yet known if they are confined to this parent material or whether a highly specialized topographic environment is necessary. The structure of the dark, massive, manganiferous layer resembles that of the pisolitic ironstone referred to above, except that in the profiles examined to date the nodules are usually larger, frequently up to 2 in. in diameter.

Although Campbell (1917) has suggested that the development of laterite is due to the input of materials carried by the ground waters from other parts of the drainage basin and that, in consequence, the rock in which it is developed is unimportant, observations on the laterites of New South Wales suggest that this is not always the case. Indeed, there is evident some considerable similarity between the composition of the original rock and that of the laterite profile which has developed on it. This is exemplified by contrasting the profiles developed on basalt and on granite. The profiles developed on basalt, with its preponderance of ferro-magnesium minerals, show a large and well-developed indurated or pisolitic horizon with a relatively meagre pallid zone. On the other hand, the profiles developed on granite, which is relatively poor in ferromagnesian minerals, contain pallid zones of considerable dimensions compared with the overlying ferruginous zone. The profiles developed on sedimentary rocks vary between these extremes, as can be seen from the examples described earlier.

Under favourable physiographic conditions, however, lateral concentration of ground water appears to have produced profile features which are increasingly independent of the rock in which the profile is developed. By contrast on rocks of favourable composition, laterite formation becomes increasingly independent of topographic concentration. In the extreme, with a favourable combination of parent rock and climate laterite might be expected to form on almost level areas where lateral concentration of ground waters would be at a minimum.

Vegetation

Relatively little direct evidence is available concerning the nature of the biological environment in which the laterites of New South Wales were formed. By inference from the climatic conditions which are considered to have been responsible for lateritization, however, and from the plant fossils found in associated deep leads, it would appear that rain forest vegetation existed during the period of laterite formation.

It is doubtful, however, if this vegetation extended on to the valley and basin laterites, where more impeded drainage conditions may have resulted in the local dominance of swamp communities. This is suggested by the occurrence of what appear to be fossil worm-holes in the lower

horizons of some of the Monaro laterites (Wolfram Hill, Jindabyne), notably those developed along broad valleys containing transported rock materials. In these more swampy situations bacterial action could have been of some importance in the precipitation of iron and manganese.

Relationships of Laterite with Other Soils

From the foregoing it would appear that under suitable topographic conditions laterites may be forming on virtually all rock materials in moist tropical to sub-tropical environments at the present time.

In the warmest environments where rock weathering is most complete the catena to be expected on most basic to moderately acid rock types would be krasnozem (e.g. red loam, latosol, &c.) on the higher slopes gradually grading into laterite on the lower slopes and flats as water-table effects become increasingly important. On very acid rocks, podzolized soils might replace the krasnozem on the higher slopes.

As slightly lower temperatures are experienced the krasnozem-laterite catena would be restricted to the more basic rocks, and the podzolic soil-laterite catena would extend to all other types.

At progressively lower temperatures a limit will be reached where the intensity of weathering would be less, and the acidity developed in the lowest catenary positions of the most basic rocks would not be sufficient to allow the formation of laterite. Under these conditions the catena would be krasnozem in the most leached upper situations, chocolate and perhaps prairie soils on the middle and lower slopes, and meadow soils on the flats. Owing to the higher acidities developed on more acid rocks, such as acid granite, gneiss, ferruginous sandstone, &c., the podzolic soil-laterite catena might be expected to develop.

In climates cooler than sub-tropical the conditions of relatively high temperatures in the deep subsoil, accompanied by water-table fluctuations that have been suggested as being requisite for laterite formation, would rarely, if ever, be achieved. These are the climates under which on all except basic rocks podzolized soils are most widely developed, and the catenas commonly encountered are podzolized soils in the higher positions, with gley podzols and meadow soils at the base of the catena in strongly acid and moderately acid situations respectively. If the ground waters were sufficiently acid or reducing to concentrate iron or manganese at the base of the catena, ortstein horizons containing these substances would develop in the gley podzols and meadow soils. These ortstein soils are, therefore, to be regarded as the cool climate equivalents of laterites, differing from them in that they lack a deep, strongly weathered subsoil containing the mottled and pallid zones. Such ortstein formations are known to be of particular importance in certain lakes and basins of the present day (Dorff, 1935).

Under similar climatic conditions, but on basic rocks such as basalt, different catenas develop. Chocolate soils and prairie soils are found in the higher positions, with meadow soils on the flats (Hallsworth, Costin, *et al.*, 1952). Since the chocolate soil environment is not sufficiently acid to allow mobilization of iron or manganese, however, lateral concentration of these elements would be restricted. A more limited formation of

ortstein by oxidation of the iron and manganese reduced in the gley horizon of the meadow soils themselves might, however, be expected to take place.

Only under still colder and moister conditions, as would obtain in alpine and sub-alpine environments, could sufficiently acid conditions develop on basalt for there to be appreciable lateral concentration of iron and manganese. In such environments alpine humus soils develop (Costin, Hallsworth, and Woof, 1952). It has been shown that the snow grass vegetation of these soils in New South Wales accumulates sesquioxides at the surface, from which iron (and manganese?) may be removed in the drainage waters as metallo-organic complexes.

Given suitable topographic circumstances these drainage waters could accumulate in basins or in shallow lakes, where the iron (and manganese) would be precipitated by bacterial oxidation with the formation of a superficial layer of ortstein over the surface of the basin or lake bed.

It has been shown by Arnio (Robinson, 1949) that under conditions similar to these iron is much more readily mobilized and removed by humus than is aluminium. This will result in a relative loss of iron from the surrounding slopes and its corresponding accumulation in the lake or basin. In contrast to lateritization, therefore, the formation of ortstein is essentially a process of iron (and manganese) accumulation *but not of aluminium*.

The essential differences between laterite and ortstein are the presence in the former soils of a horizon of sesquioxide accumulation underlain by characteristic mottled and/or pallid zones; whereas in the case of ortstein, iron and manganese have accumulated without alumina and with virtually no deeper profile differentiation except, in some cases, for the formation of gley horizons.

These criteria have led to a logical distinction between the laterites and ortsteins of New South Wales. The former soils might be considered to be the product of moist, tropical to subtropical conditions of weathering, and the latter soils in general of moist, colder conditions.

The Ortstein Profiles

The Thredbo Ortstein

Soft ortstein occurs in a meadow soil formed on detritus from gneissic granite, at 3,800 ft. on the Kosciusko road west of 'The Creel'.

0″ Brownish-black clay; granular when moist, cloddy when dry; compact and tenacious; some quartz gravel.

1′ Grey-black gravelly clay (quartz gravel); fine crumb to single grain; some brown flecks of ferric oxide present.

1′ 9″ Bluish-black gravelly clay; closed and tenacious; with large ochreous streaks and blotches of ferric oxide forming a soft ortstein; quartz and ironstone gravel present; fragments of wood, semi-fossilized and impregnated with iron.

2′ 5″ Dark grey gravelly clay (no ironstone) becoming lighter in colour into decomposing granitic colluvium.

This clearly postdates the Monaro laterites (Wolfram Hill, Jindabyne). Similar formations of soft ortstein and fossilized wood are widespread in the moister montane environments of the Monaro (e.g. Rhine Falls, the Badja, Kybean).

The Narangullen Ortstein[1]

Manganiferous ortstein occurs in a meadow soil at Narangullen, near Yass, on alluvium from Devonian tuffs and limestones.

0″	Brown loam; fine crumb; friable.
2″	Grey-brown clay loam; compact; pH 5·6.
6″	Grey clay loam; compact; containing manganiferous concretions; pH 5·7.
9″	Light grey clay loam; compact; containing increasing quantities of manganiferous concretions; pH 5·6.
1′ 3″	Yellow-grey clay; compact; abundance of manganiferous concretions; pH 5·6.
1′ 6″	Dark brown clay; many manganiferous concretions; pH 5·5.
2′ 6″	Dark grey-brown clay; few manganiferous concretions; pH 7·0.
3′	Dark grey-brown clay; containing amorphous calcium carbonate.
3′ 6″	Orange-brown clay; more amorphous calcium carbonate; pH 8·1.
4′	Rock.

The Camden Park Ortsteins

Two series of soils containing ironstone occur at Camden Park, derived from Wianamatta shales and sandstones. The Menangle series occur in areas of impeded drainage, typically flats or basins, whilst the Camden series occur in adjoining situations under conditions of free drainage.

The Menangle Ortstein

0″	Dark brown gritty silty loam, containing small ironstone nodules.
6″	Light brown sandy gravelly clay; containing an abundance of ironstone nodules (to ¾ in. diam.) together with softer concretions.
1′ 3″	Brown/orange mottled gravelly clay; nodular material less frequent.
2′	Brown/orange mottled heavy clay; with few ironstone nodules.
3′	Mottled brown/orange/red/grey clay; no ironstone present.
6′	Decomposing shale.

The Camden Ortstein

0″	Brown gravelly clay loam; containing small nodules of ironstone.
6″	Orange-brown gritty clay; ironstone nodules fewer.
12″	Orange-brown heavy clay; no ironstone nodules.
4′–6′	Decomposing shale.

These suggest that the Menangle ortstein, although partly fossil, is still being formed under the impeded drainage conditions of the present day. In contrast, the Camden ortstein is entirely fossil, since it occurs in the surface soil only, well above the level of the water-table, and has been brought to the surface by natural erosion of the soil which originally covered it.

The Barney's Range Ortstein

Hard massive ortstein is developed at the base of a ferruginous laterite at the foot of Barney's Range on the Berridale–Jindabyne road. The laterite occurs in transported materials derived from metamorphic rocks (mainly slate) which rest abruptly on hard, steeply dipping slates.

The ortstein is encountered at a depth of about 6 ft. as a hard sheet over the underlying slates, into the cracks of which it has also been deposited as nodules. It appears to have been derived from the ferruginous

[1] Profile description by H. M. Churchward.

horizon of the laterite. Since the water-table now occurs at a considerably greater depth it is itself a fossil formation.

Similar ortsteins are frequently encountered elsewhere in the drier tableland tract of the Monaro (e.g. at Carlaminda, Numeralla, Berridale, &c.). They either underlie fossil laterites or transported materials of more recent age. Although most appear to be fossil, by virtue of the present level of the water-table, some may still be forming at the present day, as for example along the Numeralla river between Numeralla and Carlaminda.

The Guyra Ortstein

Hard massive ortstein up to 15 in. thick is found covering shallow basins in the basalt of the Guyra district.

At Bald Blair, Guyra, the massive ortstein underlies most of the old lake basin (Plate VII*b*). Lumps of it protrude through to the surface in parts of the basin, but elsewhere are covered with several inches of soil. At the edge of the basin the ortstein, where covered with soil, is not so solidly cemented together, and breaks up under vigorous abrasion into the individual pisolites. The associated soils developed in topographic positions above the ortstein are typical chocolate soils (Hallsworth, Costin, *et al.*, 1952).

The profiles in which the ortstein occurs are variable owing to variations in depth of the ortstein horizon itself, but in general terms they show

0″	Grey-chocolate friable clay loam to light clay.
1′ 6″	Brown gravelly clay.
2′	Ironstone gravel with little associated clayey soil cemented in parts into massive blocks.
4′	Mottled orange/blue-grey clay containing pebbles of decomposing basalt.
5′ 3″	Decomposing basalt.

Massive ortstein (Plate XVIII) similar to this is found in several other localities in New England. At other sites the basins appear to have been subject to erosion, so that the ortstein is only encountered as a rim around what was formerly the level of the basin (Fig. 2).

On the western slopes erosion has been more severe, as at Kings Plains where only scattered lumps of the massive ironstone persist as occasional blocks along the contour, the rest of the basin at slightly lower levels being occupied by chernozemic soils, slightly gilgaied, with concretions of calcium carbonate through the profile.

This group of profiles must be compared and contrasted with the laterite profile developed on basalt as described at Fernhill. The pisolitic layer here is dark brown, heavy, and massive and rich in iron and relatively thin, whilst the Fernhill pisolitic layer is light coloured, of low density, and highly aluminous and thick. The Guyra ortsteins are so shallowly weathered that with a change in climate a chernozemic soil can develop almost around the ferruginous lumps of the old profile. Moreover, the presence of the ironstone layer going to what appears to be the edge of the old lake, with chocolate soils lying immediately up the slope from the ironstone, which itself gets thinner at its upper limit, implies

that little erosion of the country surrounding the basin has taken place since these ironstones were developed. The difference between these two groups of soils developed on basalt, as exemplified by the Fernhill laterite and the Bald Blair ortstein, are far too marked to allow them to be considered the same soil type, as can be seen by tabulating their properties below.

	Fernhill	*Bald Blair*
Colour of topsoil	Bright red	Grey-chocolate
Depth to decomposing basalt	25+ ft.	4 ft.
Character of indurated horizon	Light, bauxitic (Plate XVI)	Dense, ferruginous (Plate XVIII).
Pallid zone	Marked and kaolinitic	Absent

This is also evident from the occurrence in close proximity of laterite in the Guyra district as a residual, and of the Bald Blair ortstein in conformity with the present topography.

The Guyra ortstein appears to have been formed by some process leading to the development of a layer of iron oxide concretions in the surface of the soil material. Such a development could take place at the bottom of shallow lakes in the gently undulating surface of the basalt, the iron arising partly by reduction in the underlying soil material, but mainly by transport in streams and ground waters from the surrounding basalt.

Iron will become mobile only under highly acid or strongly reducing conditions. Such conditions are found in soils developed in basalt only with strongly acid krasnozems or with the even more strongly acid alpine humus soils. Since the shallow depth of weathering, the absence of the pallid zone, and the mildly weathered character of the associated chocolate basalt soils are the antithesis of those associated with the krasnozem-laterite catena, it follows that the Guyra ortsteins must have been formed under climates sufficiently cold for the development of soils similar to the alpine humus. Such climates, permitting the accumulation of large quantities of largely undecomposed humic substances in the ground waters, would allow removal of the iron as complexes, and favour the selective accumulation of iron rather than of aluminium in the drainage basins.

These conditions appear to be analogous to the conditions under which ironstone is reported to form in lakes of Sweden and northern Europe (Dorff, 1935), and it is suggested that the terms 'See-ortstein' or 'lake-ortstein' be used for this particular group of the ortstein-containing soils.

Ironstone in solonetzic soils

Occasional small ironstone concretions are found in the lower parts of the bleached horizon and the upper part of the B horizon of the solodized-solonetz soils found in the Pilliga and elsewhere. Their formation is probably associated with gleying on top of the impervious

B horizon. The solodized-solonetz are easily distinguished from the laterites or ortsteins described above and will form the subject of a subsequent paper.

Historical Significance of the Ironstone Soils

At least two age-groups of laterite are thought to have been preserved as fossil soils in New South Wales.

Most of the laterite profiles of the Sydney district appear to be of Miocene age, since they are usually situated on the Oligo-Miocene peneplain surface which is now dissected to varying degrees (the Sutherland, Wattamolla, and French profiles). These could hardly have been formed after the peneplain had been dissected, since the requisite water-table conditions would then no longer develop except in basins or broad valleys.

Owing to the extensive faulting which has occurred in the New England region, it is difficult to relate these laterites to Tertiary land forms (the Tingha, Emmaville, and Fernhill profiles). As for the Sydney laterites, the great depth of the profiles indicates an extremely long period of lateritization, which suggests that they were formed during the long still-stand which accompanied the extensive Oligo-Miocene peneplanation. Further evidence that the New England laterites are of considerable age is the fact that some of them underwent truncation and were subsequently covered by Tertiary stanniferous gravels (the Emmaville and Tingha profiles). This would logically occur when the Miocene peneplain was uplifted, probably at the close of the Miocene. They are of some significance in relation to the age of the basalt flows in this region, which are often regarded as belonging to one major period of volcanic activity during the Oligocene. Whilst the lower flows which underly the laterites could be of Oligocene age, the upper basalt flows which overly the laterites clearly belong to a considerably younger series (Owen, 1949), although some also show evidence of lateritization.

Nowhere in the Monaro Region have complete laterite profiles been encountered which, on physiographic and geological evidence, can be referred to the Miocene. That Miocene laterites were probably formed, however, is indicated by the occasional occurrence of scattered fragments of massive lateritic ironstone upon Oligo-Miocene peneplain remnants. Unlike the later basalts of the New England Region, all of the Monaro basalts appear to antedate the laterites and to have been extruded during the Oligocene (David, 1950).

Virtually all of the Monaro laterites which still remain *in situ* were probably formed during the Pliocene (the Jindabyne, Wolfram Hill, Bunyan, Berridale, and Bobundara profiles). This is indicated by their occurrence along the floors and adjacent slopes of Pliocene valleys which have been developed in the Oligo-Miocene peneplain (e.g. the Jindabyne, Wolfram Hill profiles). That this laterite period on the Monaro was relatively short, and/or the climate was sub-optimum for lateritization, is suggested by the relative shallowness of the Monaro profiles compared with most of those in more northern areas of the State. This is also evidenced by the fact that a larger proportion of acid, coarser

textured, readily weathered parent materials on the Monaro has been laterized than of the more basic parent materials of finer texture. The prevalence of multiple laterites (the Wolfram Hill and Bunyan profiles) similarly suggests that lateritization occurred towards the close of the Pliocene when the earth movements which culminated in the Kosciusko uplift are thought to have commenced.

TABLE 2

A Probable Chronology of Some Ironstone Formations in New South Wales

TERTIARY			
Oligocene	Probably moist, tropical to subtropical.	Monaro basalts and lower basalt flows of New England. Incipient peneplanation.	
Miocene	Moist, tropical to subtropical.	Long still-stand and extensive peneplanation. Uplift near close of Miocene.	Laterites of New England, Pilliga and West Darling, and deep peneplain laterites of Sydney. Ironstone remnants on peneplain residuals of Monaro.
Pliocene	Moist, tropical to subtropical, but becoming cooler at end of Late Pliocene.	Development of broad valleys. Accumulation of gravels on laterites in New England, followed by upper basalt flows. Commencement of Kosciusko uplift.	Laterites of Monaro, shallower laterites in valleys below peneplain surface at Sydney, upper laterites of New England, &c.
QUATERNARY			
Pleistocene	Cooler than Tertiary; moister than, and during the Kosciusko glaciations also colder than at present.	Completion of Kosciusko uplift, and commencement of new cycle of erosion and deposition. Glaciation at Kosciusko in Early and Late Pleistocene.	Ortsteins of New England and Camden, and hard ortsteins of Monaro.
Recent	Current climatic régime of comparatively low rainfall, with temperatures lower than in Tertiary and higher than during the Kosciusko glaciations.	Erosion moderating, current pedogenesis.	Ortsteins of Narrengullen and some soft ortsteins of Monaro, Camden and North Coast.

Shallow laterites developed in Pliocene valleys have also been encountered on the Southern Tablelands (Osborne, 1948), and in the Sydney district at lower levels than the more widespread Miocene formations (e.g. St. Mary's profile).

The Pliocene-Pleistocene Kosciusko uplift commenced a new cycle of erosion, which coincided with the close of the warm climatic régime of the Tertiary. Except where protected from erosion by overlying materials or by favourable physiographic situations, many of the laterites underwent truncation and the erosion products were redistributed to form secondary materials for subsequent pedogenesis.

It has been suggested (Prescott, 1931; Stephens, 1946) that the strong podzol features which now characterize the topsoils of laterites in many parts of Southern Australia are to be regarded as part of the original laterite profile. This does not appear to be necessary. In so far as the

Monaro and Sydney laterites are concerned, the upper podzolized layer is more logically interpreted as having been superimposed after lateritization as an effect of a strongly podzolizing climate. The presence of largely weathered concretions and massive laterite still remaining *in situ* within the otherwise bleached topsoil is significant in this regard (e.g. Wattamolla, Jindabyne, Wolfram Hill, and Berridale profiles).

The considerably cooler and moister climates experienced during much of the Pleistocene also favoured the development of ortstein. Iron leached from the ferruginous and mottled zones of the laterites is frequently found redeposited as ortstein near the base of the original laterite profiles (e.g. Barney's Range ortstein). The New England lake-ortsteins formed from basalt are also attributable to a colder Pleistocene climate. These lake-ortsteins indicate a probable extension of subalpine or alpine conditions to the New England region. Such conditions would have been experienced during the Kosciusko glaciations of the Early and Late Pleistocene.

The restriction of modern ortsteins to relatively few favourable ground-water situations and their much wider occurrence as fossil formations reflect the onset of more recent drier conditions since Pleistocene time.

The probable chronological relationships of the ironstone formations studied in this paper are resummarized in Table 2.

Summary

The ironstone-containing soils of New South Wales fall logically into two main groups. The laterites, which are in general fossil soils, may be divided into three sub-groups, ferruginous, bauxitic, or manganiferous, depending on the nature of the indurated horizon. The ortsteins occur as both fossil and recent formations, although one sub-group, the lake-ortstein, appears to require special conditions for its formation.

The conditions necessary for the formation of both groups are considered with regard to their relationship both to each other and to related soils.

Acknowledgements

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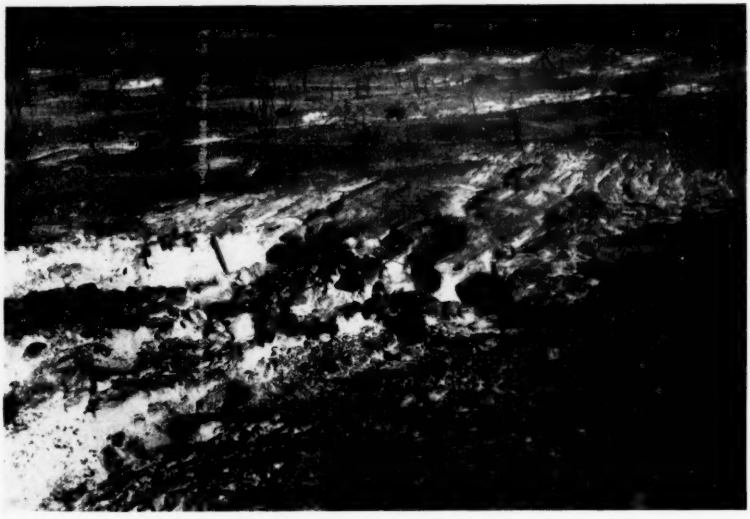
(*Received 29 February 1952*)

a. The Wattamolla profile. The indurated zone decomposing at the surface to form soil. (*Photo J. D. Colwell*)



b. The Wattamolla profile, showing current-bedding in the sandstone at the top of the pallid zone. (*Photo J. D. Colwell*)

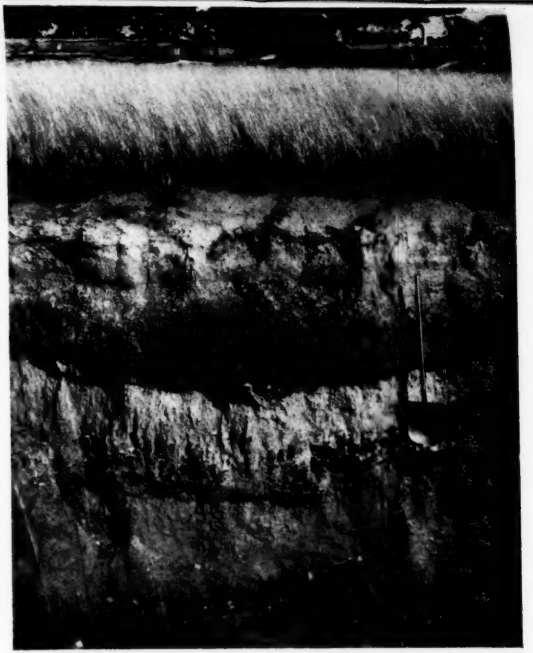
E. G. HALLSWORTH, A. B. COSTIN—PLATE I

a. The French profile, showing the indurated zone at the top and the softer mottled zone beneath. (*Photo R. Storrier*)

b. The French profile, showing mottled and pallid zones. (*Photo R. Storrier*)

E. G. HALLSWORTH, A. B. COSTIN—PLATE II

a. The Newell-Pilliga profile. The indurated, mottled, and pallid zones are all exhibited within a depth of four and a half feet. (*Photo J. D. Colwell*)



b. The Wolfram Hill profile. A multiple ferruginous laterite showing a vertical sequence of two laterite profiles (the shovel rests on the indurated ferruginous horizon of the lower profile). The podzolized top soil extending down into the upper ferruginous horizon is post-laterite.

a. The Tingha profile. A bauxitic laterite exposed by open-cut mining of stanniferous gravels. The pallid zone is extensively exposed in the foreground. The mottled zone occupies most of the face of the pit, whilst the top one to two feet is the remnant of the decomposed indurated zone. (*Photo J. D. Colwell*)

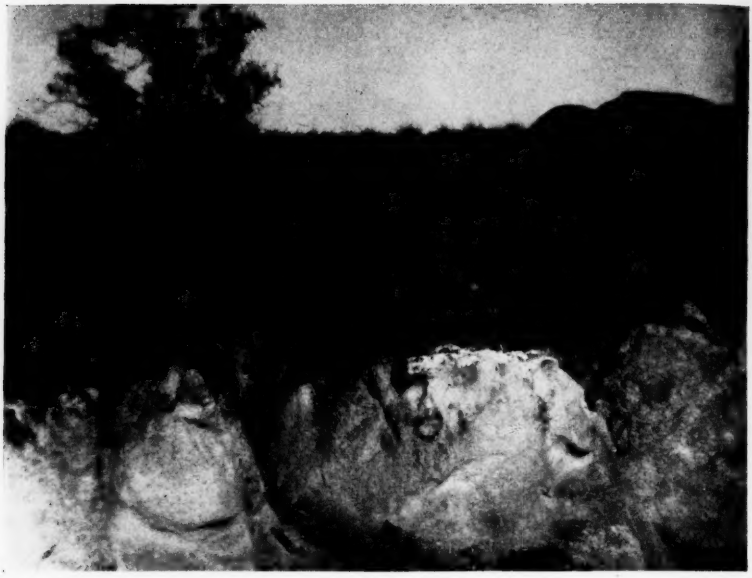
b. The Tingha profile. The silicified band ('grey billy') which extends in parts as a continuous sheet across the junction of the mottled and pallid zones.

E. G. HALLSWORTH, A. B. COSTIN—PLATE IV

a. The Emmaville profile, showing the structure of the indurated zone with the pallid zone in the foreground. (*Photo J. D. Colwell*)

b. The Fernhill profile. A bauxitic laterite. The mottled zone runs into the pallid zone, both indicated by the soil auger, which is four feet long. Two zones of larger bauxitic pisolites can be seen, one almost immediately above the handle of the auger and the other about two feet above this. (*Photo J. D. Colwell*)

E. G. HALLSWORTH, A. B. COSTIN—PLATE V



The Bobundara profile. A manganiferous laterite in which the mottled horizon is not developed.

a. The St. Mary's profile—the poly-indurated lateritized gravels. This complex of numerous indurations seamed through a more or less kaolinized mass is succeeded above by a mottled zone which is soft when cut but which quickly dries to a brick-like consistency on exposure. This layer can be seen as a wavy band just below the level of the road at the top of the photograph. (*Photo R. Storrier*)

b. The Guyra landscape, Bald Blair, showing a basin of internal drainage where lake-ortstein has been developed.

E. G. HALLSWORTH, A. B. COSTIN—PLATE VII

Indurated material from the ferruginous horizon of the Sutherland profile. Parent material Wianamatta shale. The freshly fractured surface shows a reticulate mottling of purple, with fleckings of orange, brown, and yellow, and occasionally cream. It is all fine in texture. The fleckings are soft and earthy, whilst the purple material is distinctly hard, and on decomposition gives rise to the ironstone pebbles present in the top soil. It shows no appreciable development of pisolites. (*Contrast with Plate XII*)

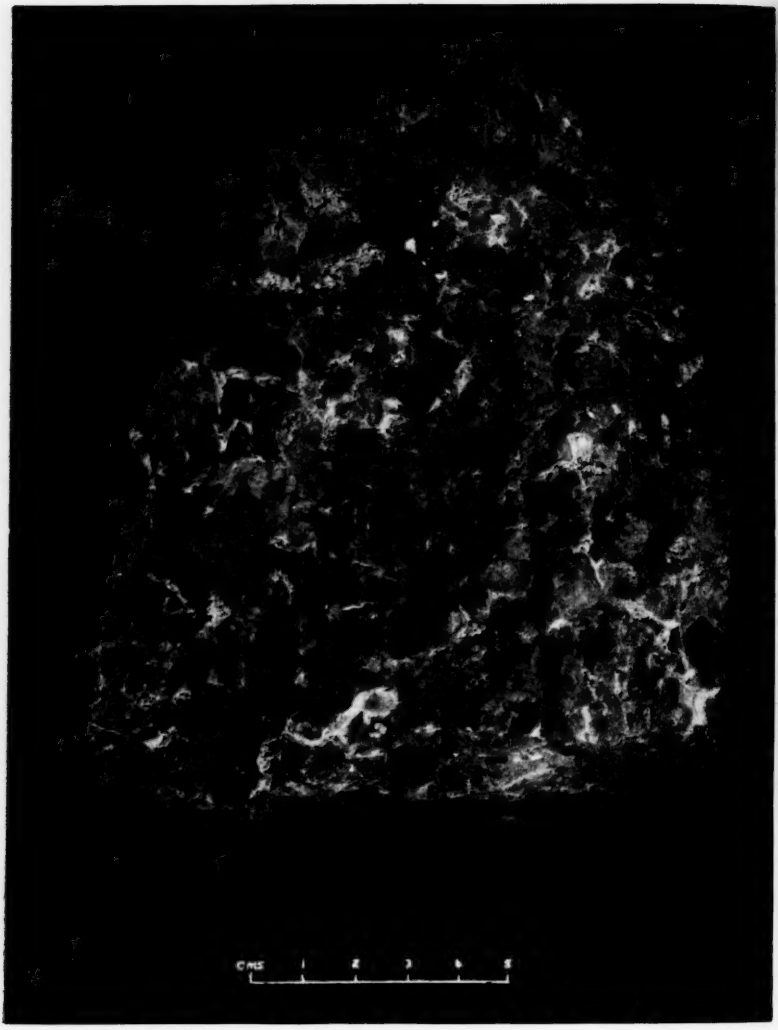
E. G. HALLSWORTH, A. B. COSTIN—PLATE VIII

Indurated material from the ferruginous horizon of the Wattamolla profile. Parent material Hawkesbury sandstone. The freshly fractured surface shows a reticulate mottling of purple, with fleckings of orange, brown, yellow, and cream, but the lighter coloured flecks are rather large. The larger grain size is obvious.

Indurated material from the ferruginous horizon from a laterite profile in National Park, about 2 miles north of the Wattamolla profile. The parent material is Hawkesbury sandstone, but the deposition of iron appears to have been much heavier. The indurated zone has in parts the appearance of ferruginous sandstone, with small cream and orange fleckings (as at lower right-hand side), whilst adjacent parts contain small pores, each lined with a thin layer of yellow-brown earthy material.

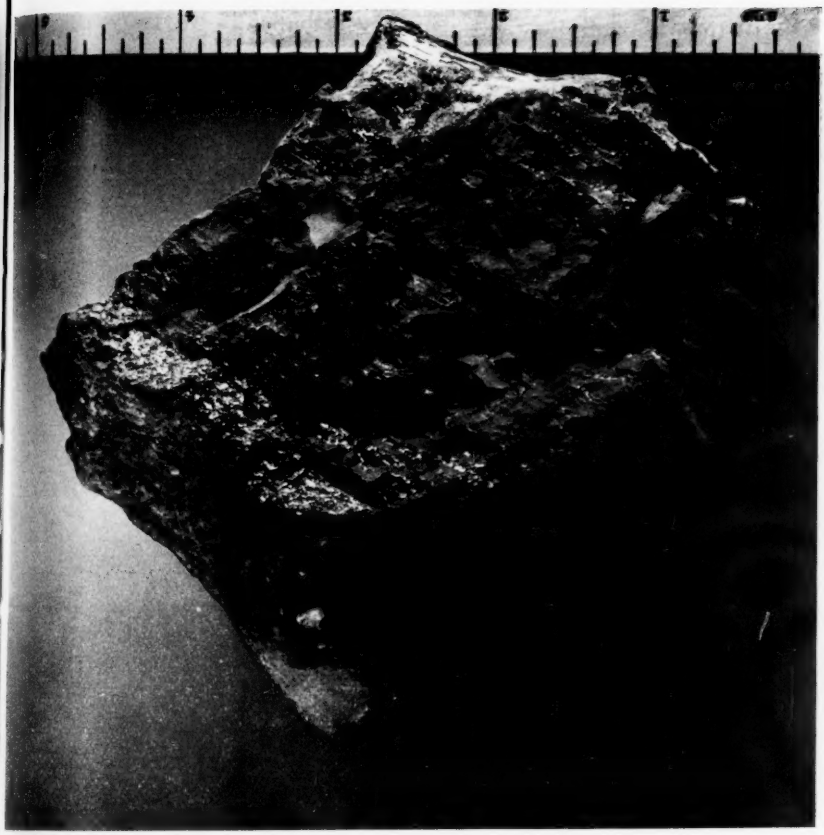
E. G. HALLSWORTH, A. B. COSTIN—PLATE X

Indurated material from the ferruginous horizon from a profile from Red Bluff, National Park. The underlying rock is Hawkesbury sandstone. The indurated material here forms large irregular-shaped masses which on fracture are found to contain large hollows of irregular shape, and may be contrasted with the regular hollows of the honeycomb pisolites of the Newell-Pilliga and Gilgandra laterites. Some banding of the different materials can be seen, particularly the harder bands of darker shade, which, as in Plates IX and X, is of dull purple colour. Note the coarse texture of the ground mass.



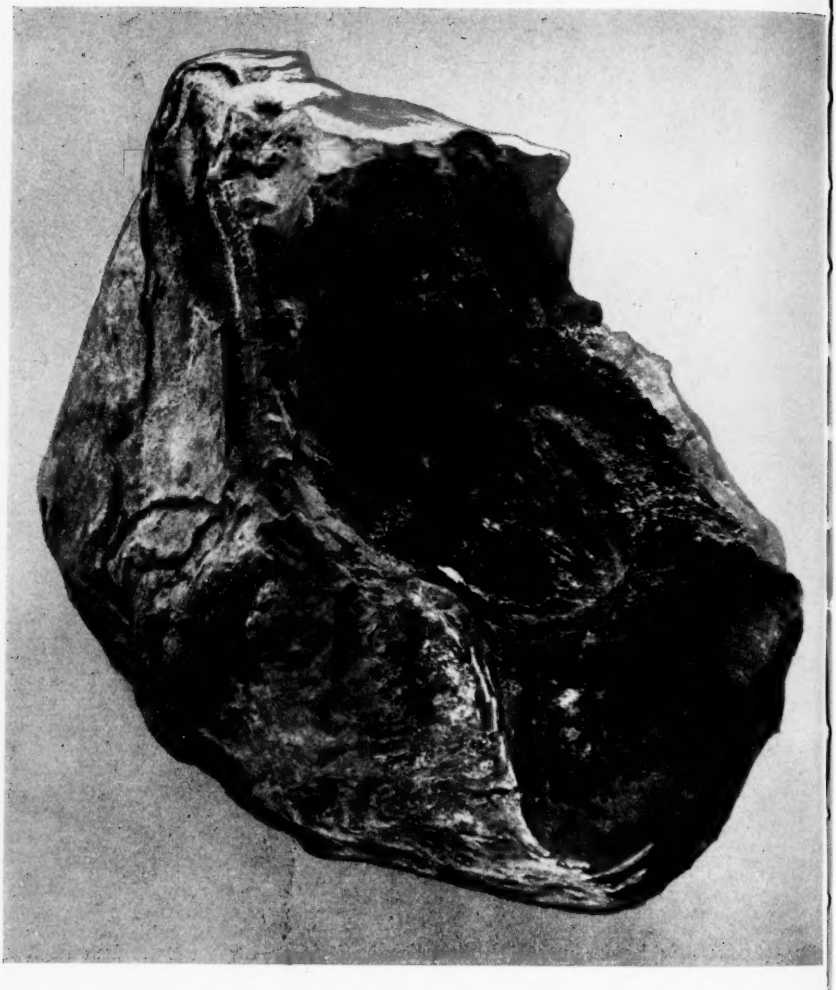
Indurated material from the ferruginous horizon of the French profile, developed through Wianamatta shale and into Hawkesbury sandstone. It is thickly studded with iron pisolites, dark red to purple when fractured, cemented together by iron oxide, which is orange-brown to yellow and shows as lighter parts on the photograph. Small pores are present in the interstices. At numerous sites examined around Sydney the indurated horizon has decomposed and the surface soil is richly strewn with the pisolites.

E. G. HALLSWORTH, A. B. COSTIN—PLATE XII



The laminated indurated horizon from the Newell-Pilliga profile. Parent material—Jurassic sands and shales. The laminae range from $\frac{1}{16}$ to $\frac{1}{8}$ inch in thickness, rather darker and not so red as those described previously. The laminae when freshly broken carry a thin black patina which on X-ray analysis appeared to be goethite (analysis by Marion Woof). The sharp junction between this horizon and the strongly indurated sandstone that immediately overlaid it can be seen in the lower portion of the photograph.

E. G. HALLSWORTH, A. B. COSTIN—PLATE XIII

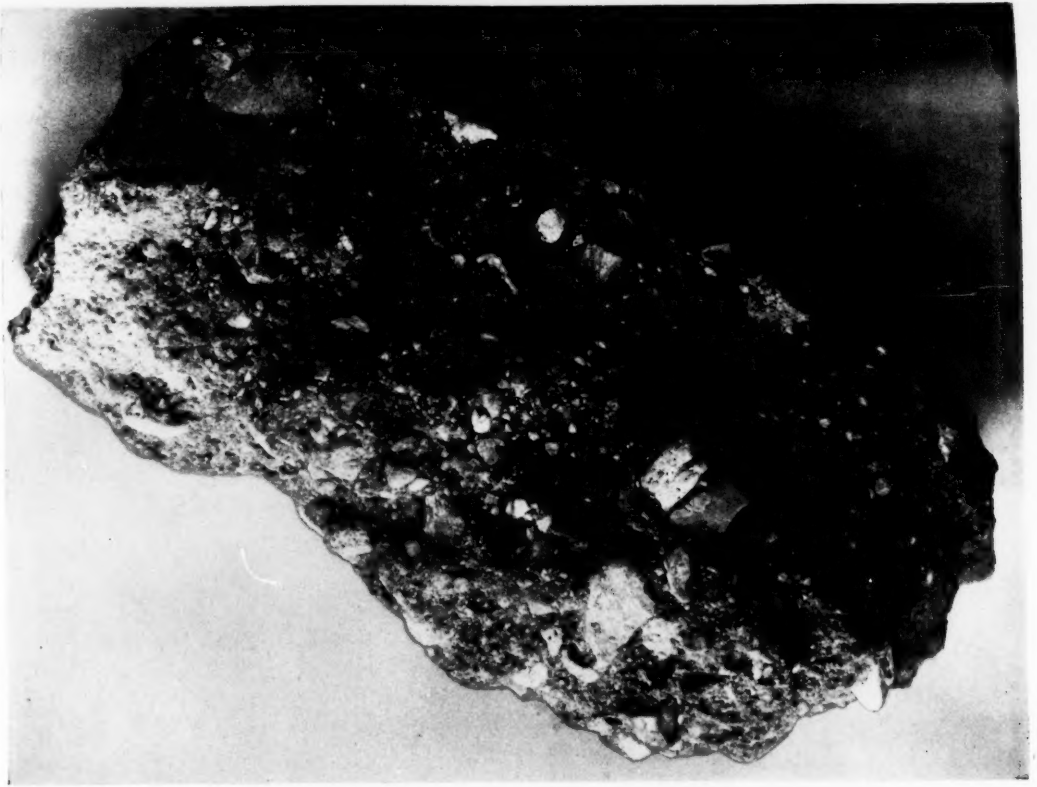


A large pisolite from the surface soil of the Newell-Pilliga profile, fractured in half before taking the photograph. The concentric layers of deposition can be seen which do not appear to be of equal density.

A large pisolite collected seven miles east of Gilgandra, developed on similar parent material to the Newell-Pilliga profile. Photographed after fracture to show the concentric nature of the deposition.

Indurated material from the Fernhill profile. Parent material basalt. This bauxitic material is bright orange-red in colour, and as in the photograph looks to be more uniform in character since the pisolites are not so different, but generally of similar character to the ground mass. (*Contrast with Plate XVII*)

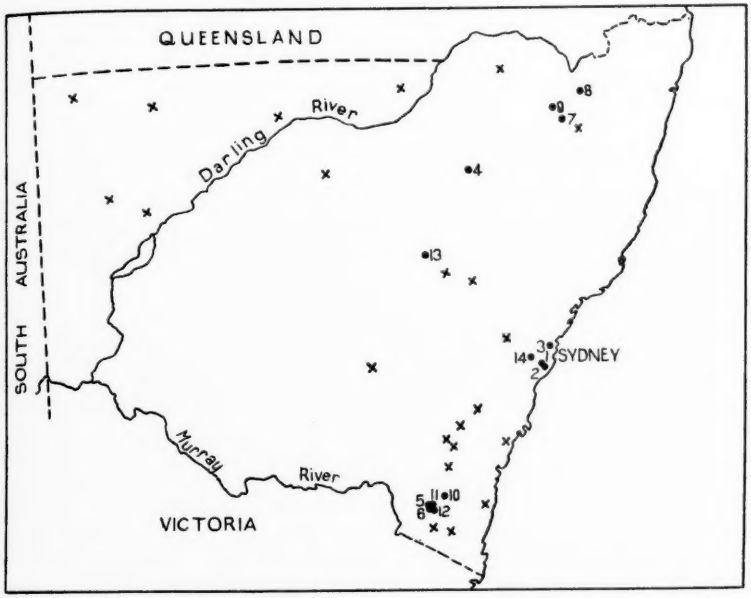
Indurated material from the Fernhill profile. Parent material basalt. This bauxitic material is bright orange-red in colour, and as in the photograph looks to be more uniform in character since the pisolites are not so different, but generally of similar character to the ground mass. (*Contrast with Plate XVIII*)



Indurated material from the lateritized river gravels at Bellata. Large pieces of quartz gravel have been cemented by a dense ground mass of iron oxide.

The ortstein horizon from the lake-ortsteins at Guyra, formed on basalt. The colour is generally darker, with dark browns, rusts, and dark purple predominating. It is highly vesicular and contains numerous small black pisolites [illegible] (Continued with Plate XVI)

SOUTH AUSTRALIA



● = Laterite profiles described in text
× = Laterite profiles observed but not described in text

1. The Sutherland profile
2. ,, Wattamolla ,,
3. ,, French ,,
4. ,, Newell-Pilliga,,
5. ,, Jundabyne ,,
6. ,, Wolfram Hill ,,
7. The Tingha profile
8. ,, Emmaville ,,
9. ,, Fernhill ,,
10. ,, Bunyan ,,
11. ,, Berridale ,,
12. ,, Bobundara ,,
13. ,, Dubbo ,,
14. ,, St. Mary's ,,

FIG. 1. Distribution of some laterites in New South Wales.

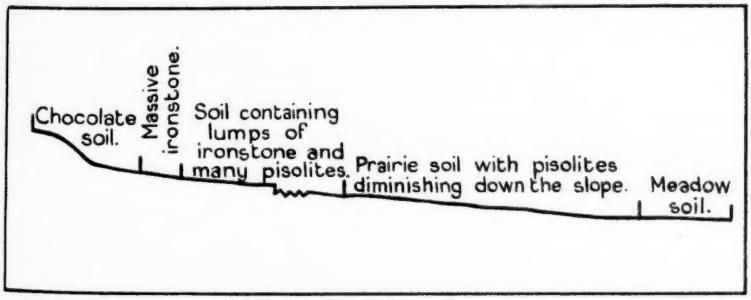

Chocolate soil.
Massive ironstone.
Soil containing lumps of ironstone and many pisolites.
Prairie soil with pisolites diminishing down the slope.
Meadow soil.

FIG. 2. Relationship of ortstein to present topography and soils, north of Experiment Farm, Glen Innes

The ortstein horizon from the lake-ortsteins at Guyra, formed on basalt. The colour is generally darker, with dark browns, rusts, and dark purple predominating. It is highly vesicular and contains numerous small black pisolites

THE CLAY MINERALOGY OF SOME SOILS FROM SPAIN AND FROM RIO MUNI (WEST AFRICA)

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THIS paper presents an account of the clay mineralogy of some soils from Spain and from West Africa, representative of the following types:

1. Dry calcareous soils (including Mediterranean *terra rossa*).
2. Andalusian black soils.
3. Iron-humus podzols.
4. Tropical loams.

In addition to the clay mineralogy of the various soils, parent materials, climate, &c., are described and an attempt is made to correlate all the available information.

Experimental

The $<1{\cdot}4\mu$ e.s.d. (equivalent spherical diameter) fraction of all the soils was separated by the usual sedimentation technique using NH_4OH as the dispersing agent. After organic-matter removal by several treatments with 20 vol. A.R. hydrogen peroxide on the steam bath the clays were dried and ground to pass through 100-mesh. Samples for differential thermal analysis were placed in a vacuum desiccator over saturated $Ca(NO_3)_2.4H_2O$ (56 per cent. relative humidity) for at least 4 days before examination.

In the Macaulay Institute d.t.a. apparatus (Mackenzie, 1952), 0·2 g. clay is heated in a ceramic specimen-holder from room temperature to 1,000° C., at a constant heating rate of 10° C./min., side by side with a 0·2-g. sample of inert material. The temperature at the centre of the inert material (the clay being analysed precalcined to 1,000° C.) and the difference in temperature as the samples heat up are automatically recorded from a chromel-alumel thermocouple system. All endothermic peak temperatures quoted refer to the temperature of the specimen at the peak, while exothermic peak temperatures refer to the temperature of the inert material at the peak.

Normal X-ray powder and oriented-aggregate techniques were employed, all samples being pretreated with glycerol for detection of montmorillonitic constituents (MacEwan, 1946). A Hilger HRX X-ray diffraction unit and 9-cm. cameras were used with $CuK\alpha$ radiation, but where iron oxides caused considerable general scattering the radiation was changed to $FeK\alpha$.

Results and Discussion

1. *Dry calcareous soils.* These soils, which receive their name from their parent material and the present climatic conditions, are distributed along the Mediterranean Sea border, through the Balearic Islands,

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Spanish Morocco, the northern and southern plains (mesetas) of Castile, and the Ebro valley. The mean annual rainfall in these regions is 300–700 mm. per annum, irregularly distributed throughout the year, while the mean annual temperature generally varies from 12° to 18° C.

Dry calcareous soils with red profiles (including Mediterranean *terra rossa*) were selected for the present study. Previous investigations (del Villar, 1937; Alvira, 1944) have shown that these have homogeneous profiles with slightly alkaline reaction (usually pH 7–8). Calcium carbonate is present throughout the profile and occasionally small amounts of sulphate and chloride occur. These soils generally yield 10–40 per cent. of red clay with a base saturation of over 90 per cent., while their cation-exchange capacity is usually 30–40 m.eq./100 g., calcium being the dominant exchangeable cation. The organic matter content is low—only about 1 per cent.

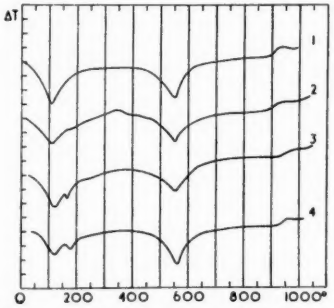

FIG. 1. Thermograms of dry calcareous soils.

Curve 1. Sample No. 187. Mediterranean *terra rossa*. Palma, Majorca.
Curve 2. Sample No. 198. Palma, Majorca.
Curve 3. Sample No. 53. Necor, Spanish Morocco. Arable land.
Curve 4. Sample No. 70. Valdepeñas, Ciudad Real. Arable land.

In Fig. 1 are shown several thermograms for clays chosen from ten soils all showing similar clay-mineralogical characteristics. These soils, identical in many places with Mediterranean *terra rossa*, present a very uniform clay mineralogy, illite being dominant, with, sometimes, a small proportion of a kaolinitic mineral. X-ray examination did not reveal the presence of any montmorillonoids.

The peptized nature of the iron compounds, stabilized by the protective action of colloidal silica in spite of the existence of calcareous materials, has been claimed to be the main factor producing the colour of *terra rossa*. The small amount of humus cannot act as a protective colloid because of its Ca-saturated condition (Reifenberg, 1947). In the clay fraction of these soils, X-ray examination showed the iron to be commonly present as the anhydrous oxide, haematite (α-Fe_2O_3), and in this connexion may be mentioned the difficulty experienced in removing free iron oxides from these soil clays by Tamm's method.

Several thermograms of these clays show two overlapping endothermic peaks in the low-temperature range, the peak at the lower temperature being the larger (see Fig. 1, curves 3 and 4). This peak system cannot be due to the presence of a clay of high cation-exchange capacity saturated with highly hydrated cations (Hendricks *et al.*, 1940) since the cation-exchange capacity is only moderate and, in addition, the peak temperatures are too low. Since chemical examination showed that Ca^{2+} and $SO_4^{=}$ are present, in all probability these low-temperature effects are due to the presence in the soil of a small amount of gypsum, which is concentrated in the clay fraction during the separation process. The peaks

correspond to the loss of 1½ mols. H_2O and ½ mol. H_2O from the gypsum molecule, resulting in the formation of anhydrite.

Briefly the minerals present in the clay fraction of dry calcareous soils are: an illitic mineral with or without a small amount of a kaolinitic mineral; anhydrous iron compounds (haematite); a small amount of gypsum.

2. *Andalusian black soils.* Within the area of dry calcareous soils, and covering a part of W. Andalusia, occur some grey to dark grey soils which differ from the surrounding ones—generally Mediterranean *terra rossa* (Albareda *et al.*, 1948). These occur on the low-lying part of the land and have a homogeneous profile. They are usually developed upon calcareous sandstone, and $CaCO_3$ is present throughout the profile while the content of soluble salts is low. They contain small amounts of Ca-saturated humus (1–3 per cent. organic matter) and are heavy soils with 30–60 per cent. of highly base-saturated clay. The

$$SiO_2 : Al_2O_3$$

ratio of the clay is high (average for ten soils, 4·47), while the cation-exchange capacity is usually over 50 m.eq./100 g. with Ca^{2+} and Mg^{2+} as the dominant cations.

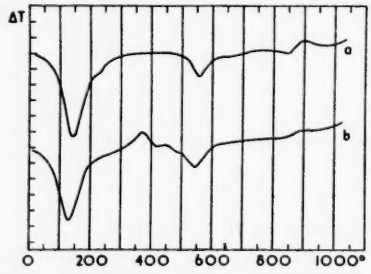

FIG. 2. Thermograms of Andalusian black soils.

Curve *a*. Sample No. 296–I. Marchena, Sevilla. Arable land.
Curve *b*. Sample No. 294. Marchena, Sevilla. Arable land.

As shown by the X-ray glycerol technique, the principal mineral in the clays of these soils was a montmorillonoid, although illite was also present. The thermograms show a large peak at low temperature, another of medium size at 500° C., and a small one at 650° C. (Fig. 2). In several of these soils calcite was found in the $<1{\cdot}4\mu$ fraction.

The large amount of montmorillonoid, with consequent large drying shrinkage, is responsible for the cracking of these soils, with the development of columnar structure, during the summer drought.

3. *Iron-humus podzols.* A study of the clay mineralogy of iron-humus podzols from Asturias, N. Spain, has recently been published (Muñoz Taboadela, 1952). These soils are developed on highly siliceous sedimentary rocks under a mean annual rainfall of 1,100–1,400 mm. and a mean annual temperature of 10–13° C. In contrast to the soils described above, these show a well-differentiated profile and, in this study, particular attention was paid to the variation in clay mineralogy down the profile.

As an example of the profile characteristics the following description may be quoted:

Location: Sama, Asturias. Altitude: 360 m.
Mean annual rainfall: 1,400 mm.; Mean annual temperature: 13° C.
Parent material: Carboniferous conglomerate of quartzite pebbles in a permeable sandy matrix.
Vegetation: Dry heath.
pH values: 4·2–6·1, increasing with depth.

Horizon	*Depth*	*Description*
A_0, A_1	0–13 cm.	Dark raw humus, sandy; clay content 7·2%.
A_2	13–35 cm.	Greyish, bleached gravel and sand; eluvial horizon; clay content 4·8%.
B_h	35–41 cm.	Black layer of humus accumulation; gravel and sand; clay content 20·2%.
B_s	41–67 cm.	Reddish brown loam with coarser materials; clay content 22·6%.
B_s–C_1	67–97 cm.	Parent material mixed with reddish clay; highest clay content, viz. 27·0%.
C_1	97 cm.+	Quartzite conglomerate with sandy matrix; some illuviated clay.

The predominant clay minerals found in these podzols were dioctahedral illite and kaolinite, montmorillonoids being absent. Gibbsite (γ-$Al_2O_3 . 3H_2O$) and goethite (α-$Fe_2O_3 . H_2O$) were present as accessory minerals. Because of the small amount present, detection of the gibbsite by X-rays was difficult, as its most intense reflections are very close to some of illite and kaolinite, both of which were present in considerable quantity.

The detection of gibbsite by d.t.a. was, however, considerably easier because, although the endothermic effect at 320° C. (Fig. 3) might have been due to gibbsite or to limonite, it has been possible to distinguish between these two by checking the solubility in NaOH, limonite being insoluble. For this purpose, 1 g. clay was treated with 50 ml. 5 per cent. NaOH solution for 20 minutes at 95° C.—a treatment which does not appreciably affect the clay minerals present. The absence of the endothermic effect at 320° C. on the thermogram of the extracted clay and the presence of Al^{3+} in the extract confirmed the presence of gibbsite in the clay.

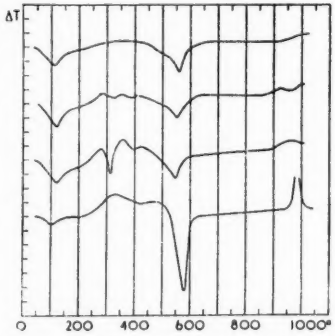

FIG. 3. Thermograms of several horizons of an iron-humus podzol. Sample No. 558 III, IV, V, and VI. Sama, Asturias.

From top to bottom, horizons B_h, B_s, B_s–C_1, and C_1.

The clay mineralogy of this podzol on sedimentary siliceous materials is on the whole very similar to that of podzolic soils on limestone and granite in America (Alexander *et al.*, 1939), of podzols on granite studied by Sedletsky (1945), and of the podzol on sandy material investigated by van der Marel (1949).

The composition of the clay fraction was found to vary from horizon to horizon down the profile, the general variation being similar for all those examined, although the one described above showed the largest changes. Some thermograms are shown in Fig. 3, and X-ray photographs have been previously published (Muñoz Taboadela, 1952). Quantitative determinations of kaolinite, gibbsite, and goethite in each sample were carried out by d.t.a., while X-ray data were used for quantitative determination of quartz.

The variation in clay composition down the profile is shown in Fig. 4, where the ordinate represents the various podzol horizons and the abscissa shows, from left to right, the percentages of quartz, kaolinite, illite, and hydrous oxides. The eluvial A_2 horizon showed essentially kaolinite and illite with some quartz, the quartz disappearing and the illite increasing towards the horizons immediately below. In the illuvial horizons, therefore, illite predominated over kaolinite, less than 15 per cent. of kaolinite being present in the layer of sesquioxide accumulation B_s. The crystalline hydrous oxides gibbsite and goethite were also found in these layers—about 5 per cent. of each in horizon B_s and 5–10 per cent. of gibbsite with 5 per cent. goethite in horizon B_s–C_1. The small amount of clay illuviated into horizon C_1 was essentially kaolinite.

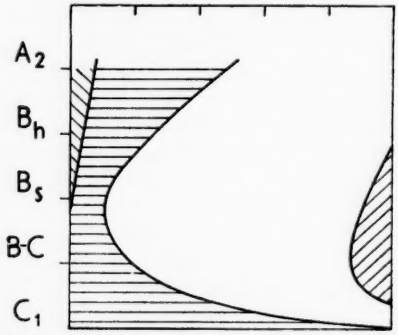

FIG. 4. Iron-humus podzol. Sample No. 558. Sama, Asturias. Ordinate, podzol horizons; abscissa, beginning from the left, approximate percentages of quartz (diagonal shading), kaolinite (horizontal shading), illite (blank), and hydrous oxides (diagonal shading).

(Graph showing the clay composition of several horizons.)

X-ray photographs of the clay from horizon A_2 showed the 10 Å basal spacing of the illite to be asymmetrical and broadened towards higher spacings. According to MacEwan who also found this type of illite in A_2 horizons of podzols developed on micaceous schists (1948), this asymmetrical reflection is due to more or less random hydration between the mica sheets (1949). The illite present in the B horizons gave a sharp 10 Å reflection.

As regards parent material, X-ray analysis of milled samples showed the rock to be free from all micaceous and clay minerals except for a minute trace of kaolinite (< 0·5 per cent.). The principal mineral was quartz with small amounts of other light minerals and some heavy ones. The sedentary character of this profile was confirmed by the presence of the same heavy mineral assemblages (mainly zircon, tourmaline, and rutile) in the parent material as in the soil horizons (Edelman, 1936; Marshall, 1940).

Considering the above data on the nature of the parent material and the concentration of illite in the B horizons, it would seem that the formation of illitic materials occurs in these illuvial horizons. Indeed, considering the conditions prevailing in each horizon of the profile, only in these accumulation layers could the conditions be suitable for the formation of lattices not completely leached of bases—the pH values and the percentage base saturation both being higher than in the horizons above. Conversely the eluvial acid conditions in the A_2 layer are more favourable for the formation of kaolinite (Nagelschmidt, 1944). It would appear, therefore, that at least part of the kaolinite in this soil is formed by the weathering of illite (Jackson *et al.*, 1948) in the eluvial horizons.

The following table summarizes the main conclusions:

TABLE I

Horizon	*Clay mineralogy*	*Remarks*
A_2	Kaolinite and asymmetrical-10 Å-reflection illite	Weathering of illite to kaolinite
B_h, B_s, and B_s–C_1	Sharp-10 Å-reflection illite dominant, and kaolinite. Hydrous oxides gibbsite and goethite	Formation of illite
C_1	Essentially kaolinite	Weathering of parent material
C	Parent material free from micaceous and clay minerals except for a minute trace of kaolinite	. .

4. *Tropical loams.* These soils, which came from Rio Muni, West Africa, have been described elsewhere (Alía *et al.*, 1952). In some of them lateritic horizons of loose concretions were found, and their clay mineralogy, as might be expected from their origin, was different from those already described. The following is a typical occurrence:

Location: near Mikomeseng, Rio Muni. Mean annual rainfall: 2,100 mm. Mean annual temperature: 28° C. Parent material: acid migmatitic rock. Vegetation: forest.

The thermograms in Fig. 5 show that the clays from these soils consisted mainly of a mineral of the kaolinite group (principal endothermic effect at 565–570° C.). The asymmetrical shape of the peak suggests metahalloysite rather than kaolinite (Dean, 1947; Bramão *et al.*, 1952), and this was confirmed by electron-microscope examination which showed the tubular crystals of metahalloysite, together with unrolling forms. The tubes were up to 1·4μ in length and up to 0·13μ in external diameter, but the ratio between the two was not constant.

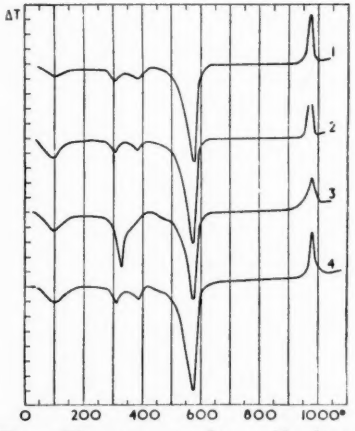

FIG. 5. Thermograms of several horizons of a tropical loam. Sample No. 515 I, Ia, II, and III. Acurenam, Rio Muni (W. Africa). Curve No. 3, lateritic horizon of loose concretions.

Summarizing the results—the dominant clay mineral was metahalloysite (70–90 per cent.) with the accessory minerals gibbsite (3–18 per cent.) and goethite (*c.* 3 per cent.). The percentage of gibbsite was somewhat higher in the clay fraction of the lateritic horizons of loose concretions.

Summary

Each of the soil types studied showed distinctly different trends in its clay mineralogy—the factors determining soil formation also determining the mineralogical constitution of the clay fraction. The results are summarized in Table 2.

TABLE 2

Soils	*Parent material*	*Clay minerals*		
		Dominant	*Accessory*	*Distribution through profile*
Dry calcareous soils (including Mediterranean *terra rossa*)	Calcareous	Illite	Kaolinite Haematite Quartz (Gypsum)	Regular
Andalusian black soils	Calciferous sandstone	Montmorillonite	Illite Quartz (Calcite)	Regular
Iron-humus podzols	Highly siliceous sedimentary rocks	Illite or kaolinite depending upon horizon	Quartz Gibbsite Goethite	Irregular
Tropical loams	Mainly acid rocks	Metahalloysite	Gibbsite Goethite	Irregular

Acknowledgements

The author desires to express his gratitude to the Director, Dr. D. N. McArthur, for the facilities provided for carrying out this work; to Dr. R. C. Mackenzie and Dr. G. F. Walker for their advice on the interpretation of the thermograms and X-ray photographs respectively; and to the Consejo Superior de Investigaciones Científicas for the grant during tenure of which this work was performed.

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(Received 21 July 1952)

THE PEDOLOGICAL SIGNIFICANCE OF TITANIUM[1]

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LITERATURE on the titanium content of soils dates back to 1891 when Dunnington collected soil samples from many parts of the world and analysed eighty specimens (Joffe and Pugh, 1934). McGeorge (1912) and Robinson (1914) reported on the titanium content of some normal Hawaiian soils and some American soils, respectively. Joffe and Pugh presented a compilation of data on titanium and other constituents of soils of various parts of the world from the reports of various workers.

An examination of the data presented reveals that

(1) the titanium content within the various soil zones varies from as low as 0·27 per cent. to as high as 4·04 per cent.—variations which Joffe and Pugh sought to relate to the composition of the parent material;

(2) the titanium content of soils in the tropics, especially lateritic soils and laterites, with a few exceptions is higher than that in the soils of temperate climates.

Few systematic studies have been made on the soil colloids on a profile basis and practically none on a horizon basis. Steinkoenig (1914) did some work on the distribution of TiO_2 in various fractions of a number of soils and showed that the TiO_2 content is highest in the clay and fine silt fractions, and the data collected by Joffe and Pugh on the distribution of SiO_2 and R_2O_3 at arbitrary depths give some indications of pedological significance, namely,

(1) in the podzolic process of soil formation TiO_2 seems to accumulate in the B horizon;

(2) in the lateritic process of soil formation the accumulation seems to be in the A horizon.

This was also observed by Joffe (1949).

Nothing has yet been reported regarding the TiO_2 status of clay fractions under varying pedogenic processes, but a comparison of the vertical distribution of TiO_2 of the soils and the corresponding clays of some podzolic and lateritic soils of the U.S. as presented by Robinson and Holmes (1924) indicates that under the podzolic process the TiO_2 content seems to be higher in the A-horizon clay than that in the B-horizon clay, and the reverse under the lateritic process. This, however, is nothing more than a general indication.

It was therefore decided to study the profile distribution of TiO_2 in the clay fractions of different horizons of some South Australian soils—which were grouped as Red-brown earths (R.B.E.), Hydrohalogenic soils (solodized) (Y.B.E. and P 1/S), and Rendzinas (BL.E.). TiO_2 was

[1] Based on a portion of a Ph.D. thesis accepted by the University of Adelaide, 1951.

determined colorimetrically, and the analytical results are shown in Table 1.

TABLE 1

Distribution of TiO_2* *in the Clay Fractions*

Genetic Group	*Soil type*	*Depth in inches*	*Horizon*	TiO_2%	$\frac{SiO_2}{R_2O_3}$
Red-brown earths	R.B.E. 1/SL	9–11	A_{2b}	1·77	2·26
		12–27	B_1	1·19	2·13
		31–48	B_2	1·17	2·22
	R.B.E. 2/SL	3½–4½	A_2	1·49	2·30
		5½–13	B_1	1·11	2·17
		13–17	B_{2a}	1·13	2·20
	R.B.E. 2/SCL	0–3	A_1	1·41	2·21
		5–9½	B_1	1·09	2·19
		12–14	B_{2a}	1·02	2·24
Hydrohalogenic soils	Y.B.E. 1/S	6–12	A_2	1·95	2·65
		13–22	B_1	1·25	1·95
		26–38	B_2	1·19	1·90
	Y.B.E. 2/LS	4–5	A_2	1·55	2·24
		5–15	B_1	1·23	2·16
		22–30	B_2	1·11	2·17
	P 1/S	8½–14	A_2	2·79	2·78
		16–21	B_1	1·35	1·95
		22–39	B_2	1·19	1·93
Rendzinas	BL.E. (A)	0–7	..	1·11	3·05
		9½–15½	..	1·10	3·00
		20–29	..	1·09	3·15
	BL.E. (B)	0–3½	..	1·13	3·02
		15–28	..	1·00	3·16
		90–108	..	1·06	3·07

* Expressed on ignited clay.

The results show that

(1) in the rendzina soils the TiO_2 content was constant from the surface downwards;

(2) in the red-brown earths and the hydrohalogenic soils, which displayed podzolic characters in varying degrees, the TiO_2 content was invariably much higher in the A_2 horizon than that in the B horizon;

(3) the contrast between TiO_2 contents of the A_2 and the B horizons in the different profiles is related to the degree of podzolization as indicated by the SiO_2:R_2O_3 ratio of the clay fractions given in the last column of the table.

Summary

The above observations suggest that the distribution of titanium in the clay fractions of different horizons of a soil profile may be a significant index for the classification of soils, as the investigation shows that under the operation of a podzolic process TiO_2 accumulates in the A-horizon clay, and the relative accumulation varies with the degree of the podzolization. It is assumed, by inference, that under a lateritic process accumulation of TiO_2 would be found in the B-horizon clay.

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THE NITRIFYING BACTERIA: A REVIEW

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SALTPETRE (potassium nitrate) began to be regarded as a useful substance in the fourteenth century, when gunpowder was first used in Europe, and for the next 500 years it was collected, mainly for the manufacture of gunpowder but also for pickling meat, from the places where it naturally occurred in abundance. 'Earths moistened and manured with the excrements of animals; or old walls, and the plaster of ruined buildings, impregnated with the excrementitious *effluvia* of the animals that inhabited them' (Boerhaave, 1753) were good sources of saltpetre; so, too, were the walls of cellars, the earth of disused graveyards, and burial mounds (Niklewski, 1910). In quite recent times the sites of abandoned villages in hot countries like India and Egypt were bought for the sake of the saltpetre in and below the houses.

All the sites in which saltpetre was found were protected from the sun and rain, and contained large quantities of nitrogenous organic matter. So, when Napoleon wished to have saltpetre made in France for gunpowder, because the blockade had cut off the supply of imported nitrate, nitre-heaps were made in imitation of the natural sites (Boussingault, 1844). Heaps of a mixture of earth, manure, and chalk were built inside wooden sheds; they were watered with urine and waste water, and either aerated by pipes or turned from time to time. After about 2 years the crude saltpetre was extracted from the heaps with hot water.

The Isolation and Nature of Nitrifying Bacteria

In view of the association of saltpetre in nature with large quantities of organic matter, it was very surprising, when the bacteria that formed nitrate were at last isolated, that they turned out to be autotrophic, i.e. independent of organic matter.

In 1877 Schloesing and Müntz showed that the oxidation of ammonia to nitrate in sewage was a biological process. Warington (1878) found that nitrate formation in soil was a biological process, and that ammonia was the starting-point for nitrification. Later (1891) he described two kinds of bacteria obtained by inoculating liquid media with soil. One kind oxidized ammonium salts to nitrite; the other kind oxidized nitrite to nitrate, and did not oxidize ammonia. Both processes were found to take place in liquids containing no organic matter, and neither species of bacterium could be grown on gelatine. Frankland and Frankland (1890) also described a small oval bacterium, which oxidized ammonia to nitrite in inorganic media.

But the nitrifying bacteria were first isolated in pure culture by Winogradsky (1891), by the use of poured plates of silica gel, and to him is due the discovery of their true nature. The nitrifying bacteria are autotrophic; that is to say, they are entirely dependent for energy on the oxidation reaction they carry out. They cannot use the breakdown of

organic materials as a source of energy, as the ordinary heterotrophic bacteria do.

For the ammonia-oxidizers the source of energy is the reaction:

$$2NH_3+3O_2 \rightarrow 2HNO_2+2H_2O+79 \text{ Cals.}$$

and for the nitrite-oxidizers:

$$HNO_2+\tfrac{1}{2}O_2 \rightarrow HNO_3+21{\cdot}6 \text{ Cals.}$$

The only source of carbon which the nitrifiers can use for the building up of their cell substance is carbon dioxide (Godlewski, 1895).

The Efficiency of the Nitrifiers

The nitrifying bacteria form much more than traces of nitrite and nitrate in liquid cultures; Warington (1879) found that about 94 per cent. of the ammonia supplied to mixed cultures was converted to nitrate.

A culture is best started with a low concentration of substrate (M/200 ammonia, or M/70 nitrite: Meyerhof, 1916); but nitrification can be stepped up by repeated small additions of ammonia or nitrite, until the end products become sufficiently concentrated to stop the reaction. This occurs at a concentration of about 2 g. nitrite nitrogen, or 5 g. nitrate nitrogen, per litre in liquid cultures (Gibbs, 1919); but Müntz and Lainé (1907), using a continuous-flow apparatus filled with peat, were able to step nitrification up till they obtained an effluent containing 4·7 per cent. calcium nitrate (about 10 g. nitrate nitrogen per litre).

But the amount of cell substance formed by the nitrifiers is very small in relation to the amount of ammonia or nitrite oxidized; estimates have been made by various authors of the ratio nitrogen oxidized/carbon assimilated: values obtained for ammonia oxidation were: 35 (Winogradsky, 1890), 33 (Hes, 1937), and 70 (Engel, 1929); and for nitrite oxidation: 100 (Meyerhof, 1916) and 76 (Nelson, 1931). This explains why nitrifiers grow so slowly in culture (Winogradsky, 1890), and why their numbers in soil are of the order of thousands, not millions, per gramme (Ziemięcka, 1932).

Morphology and Classification of the Nitrifiers

Ammonia oxidizers

1. *Nitrosomonas.* A species of this genus was the first nitrifier to be isolated (Winogradsky, 1891), and isolations of the same or related species have been made by several later workers (see Kingma Boltjes, 1934, 1935, for work up to that date). All accounts of *Nitrosomonas* agree that it forms a zoogloea round the carbonate particles in the usual culture medium, and that it has oval cells, about 1·5 microns long and 1 micron across. It does not form spores. The colonies on silica-gel plates are very small, only about 100 microns in diameter; Winogradsky (1904) and Kingma Boltjes (1935) show photographs of characteristic colonies.

Some strains form a motile stage easily (Jensen, 1950 *a*), and some only occasionally or not at all (Meiklejohn, 1950). The reaction to Gram

staining has been reported as positive (Heubült, 1929), weakly positive (Jensen, 1950 *a*), and negative (Meiklejohn, 1950).

Bömeke (1951) considers that there are at least two species of *Nitrosomonas*:

(*a*) *N. europaea*. The ratio of nitrogen oxidized to carbon assimilated has a value of about 35 in this species. It forms a motile form only rarely, and it resists exposure to 60° C. for 5 minutes, and will survive in 3 per cent. sodium chloride. Bömeke thinks that the strains isolated by himself (1946), by Winogradsky (1890) at Zürich, and by Kingma Boltjes (1934) belong to this species. It seems probable that the strain isolated by Meiklejohn (1950) should also be included in *N. europaea*.

(*b*) *N. oligocarbogenes*. The ratio nitrogen oxidized/carbon assimilated is about 70. This species is Gram-positive, forms a motile stage easily, is less resistant to heat than *N. europaea*, and does not survive in 1·4 per cent. sodium chloride.

Bömeke thinks that Winogradsky's strain from Gennevilliers (1904) and those isolated by Heubült (1929) and Engel and Skallau (1937) belong to this species; it is possible that the strain isolated by Jensen (1950 *a*) also belongs here.

Another species, *N. monocella*, was isolated in North America by Nelson (1931).

2. *Nitrosococcus*. Strains classified in this genus were isolated by Winogradsky from South American and Australian soils (1904), and by Bonazzi (1919) from North American soils. They are large cocci, 1·5 to 2 microns across; they do not form zoogloea, and are not motile.

The three genera which follow, *Nitrosospira*, *Nitrosocystis*, and *Nitrosogloea*, were all obtained in culture by the later technique of Winogradsky and Winogradsky (1933), which consists in placing small particles of soil on the surface of silica-gel plates, and picking off the growth that appears; it is not designed to give pure cultures.

3. *Nitrosospira*. Cultures of this genus were obtained by Winogradsky and Winogradsky (1933) from soils from France and Nova Zemblya. The cells in young cultures were long flexible spirals, resembling *Leptospira*; the largest seen were 15 to 20 microns in length. In old cultures only cocci could be seen, which were presumably the broken fragments of the spirals.

4. *Nitrosocystis*. The first organism which Winogradsky placed in this genus was isolated by Romell (1927) from Swedish forest soils. It differed from all other nitrifiers (except *Nitrocystis*), because it produced visible hard masses, 0·5 mm. and more in diameter, on silica-gel plates. According to Imšenecki (1946), it is doubtful whether this species is really a nitrifier; he tried the same method of cultivation, and found that *Nitrosomonas* first appeared on his plates, but was later overgrown by a myxobacterium, *Sorangium symbioticum*, which is not a nitrifier, and which forms hard fruiting bodies closely resembling the masses described by Romell.

The other species which Winogradsky (1933) included in *Nitrosocystis* were quite different; they were the organisms from Zürich and Java which he had originally classified as *Nitrosomonas*. He reclassified them

on the grounds that they formed hard colonies on silica gel, whereas *Nitrosomonas* should form soft colonies. Kingma Boltjes (1935) threw much doubt on this reclassification, by obtaining both hard and soft colonies in cultures of *Nitrosomonas* derived from single-cell isolates. Meiklejohn (1951 *b*) considered that the appearance of hard or soft colonies on a plate depended on the density of the silica gel, and on whether the colony was in the gel or on the surface. It is extremely probable that *Nitrosocystis* in this sense is identical with *Nitrosomonas*.

5. *Nitrosogloea*. Three species of this genus were obtained by H. Winogradsky (1937) from activated sludge. They form a dense zoogloea, in which the cells are arranged in tetrads or chains; motile forms have not been described.

Nitrite oxidizers

1. *Nitrobacter*. There appear to be two species. *N. winogradskii* was first isolated by Winogradsky (1891) and has been isolated by several workers since (see, for earlier work, Kingma Boltjes, 1935, also Engel and Skallau, 1937, and Meiklejohn, 1952 *a*). This species has oval cells, about 1·0 by 0·8 micron, non-spore-forming, non-motile, and Gram-negative. On nitrite agar it forms colonies about 200 microns in diameter; deep colonies are lentil-shaped, surface colonies circular, soft, and transparent. A motile species, *N. agile*, has been described by Nelson (1931).

The other genera of nitrite-oxidizers were obtained by the technique of Winogradsky and Winogradsky (1933); they are:

2. *Nitrocystis*. This genus formed large hard bodies on silica-gel plates; the bodies grew to be 2·5 mm. in diameter (H. Winogradsky, 1937). Young colonies, when crushed, were found to consist of a mass of small clusters of cells, embedded in a gelatine matrix.

3. *Bactoderma*. This was the name given by Winogradsky (1933) to the thin film of cells which sometimes appears on the surface of cultures on liquid media containing nitrite. It is very doubtful whether it is a nitrifier (Kingma Boltjes, 1935).

Physiology of the Nitrifiers

Only two genera, *Nitrosomonas* and *Nitrobacter*, have been studied in detail; there is one study of the physiology of *Nitrosococcus* sp. (Bonazzi, 1919, 1921, 1923).

Reaction to light. The nitre heaps of 150 years ago were protected from the sun by wooden sheds (Boussingault, 1844), as saltpetre was known to be formed more quickly in the shade. Warington (1878) found that liquid cultures nitrified more quickly in a dark cupboard than on the open bench. It is the usual practice to keep bacterial cultures in the dark, and the question of the influence of light was not raised again until Dhar and his co-workers (Tandon and Dhar, 1934) put forward the hypothesis that nitrification in tropical soils was a photochemical, not a biological, process. However, Fraps and Sterges (1935) and Waksman

and Madhok (1937) showed that no nitrate was formed in sterilized soil exposed to sunlight, and that, in fresh soil, nitrification was quicker in the dark.

Adherence to solid particles. Warington (1884) observed that the sediment at the bottom of liquid cultures of nitrifiers was a better inoculum than the supernatant; and Frankland and Frankland (1890) and Winogradsky (1890) observed that the supernatant of a nitrifying culture is quite clear. The liquid media used for nitrifiers contain an excess of calcium or magnesium carbonate, and it is very noticeable that all the bacteria are found adhering to the carbonate particles. When the motile stage of *Nitrosomonas* appears, the cells leave the chalk particles and swim freely in the supernatant, which becomes faintly cloudy (Winogradsky, 1890). *Nitrosomonas* strains which do not form a motile stage can be released into the supernatant by blowing carbon dioxide through the cultures (Meiklejohn, 1950). If a drop of the sediment in a culture is stained with an acid stain, the chalk particles are dissolved, and the cells of *Nitrosomonas* are seen to be embedded in a matrix, forming a zoogloea (Kingma Boltjes, 1935). It is probable that nitrifiers in soil adhere to the soil particles, as it was shown by Lees and Quastel (1946) that only ammonia adsorbed on to the surface of soil particles was oxidized to nitrate in their percolation apparatus.

Effect of aeration. As might be expected of organisms which depend for their very life on an oxidation reaction, the nitrifiers are strictly aerobic, and nitrification in culture can be increased by circulating the liquid medium over solid particles (Boullanger and Massol, 1904; Müntz and Lainé, 1907; Lees, 1951). Nitrification is suppressed if air diluted with nitrogen is used to aerate soil samples (Amer and Bartholomew, 1951).

Effect of acidity. Nitrification is said not to take place in very acid soils (Arnd, 1919). The optimum reaction for *Nitrosomonas* sp. was found by Meyerhof (1916) to be pH 8·5 to 8·8, and for *Nitrobacter* sp. pH 8·3 to 9·3. (The cultures were sent to him from Winogradsky's laboratory.) Winogradsky and Winogradsky (1933) described six strains of *Nitrosomonas* with different pH optima ranging from 6·0 to 9·0, and seven of *Nitrobacter*, with pH optima from 6·3 to 9·4.

Substrates for growth and respiration. The essential reactions on which the life of the nitrifiers depend have been mentioned above. Meyerhof (1916) studied the oxygen uptake of cultures of nitrifiers, and found that the oxygen taken up could all be accounted for by assuming that the oxidation of ammonia to nitrite, or nitrite to nitrate, was the only reaction taking place.

However, in 1939 Bömeke showed that very thick suspensions (concentrated by centrifuging) made from old cultures of *Nitrosomonas* and *Nitrobacter* gave a measurable, but very small, oxygen uptake. He attributed this to endogenous respiration, in which the cell contents, synthesized with the help of the energy derived from the oxidation of ammonia or nitrite, were being used as a substrate. The small endogenous oxygen uptake was slightly increased by the addition of certain organic substances (sodium acetate, yeast water, broth, soil extract,

calcium glycerophosphate, lactate, and peptone, but not asparagin or urea).

Quite a different autotroph, *Thiobacillus thiooxidans*, which depends for energy on the oxidation of sulphur, has been found to have a small endogenous respiration in the absence of sulphur (Vogler, 1942).

Inorganic nutrients required. As well as carbon dioxide and either ammonia or nitrite, the nitrifiers are known to need calcium, phosphorous, magnesium, and iron.

Calcium is necessary for *Nitrosomonas*; about 1 mg. per litre is needed for optimum growth (Kingma Boltjes, 1935). Phosphate and magnesium are essential for *Nitrosomonas* and *Nitrobacter* (Bömeke, 1949), but the minimum amounts required for growth are very small (Meiklejohn, 1952 *c*). The absolute requirements for iron are very small, but nitrification is stimulated in pure cultures by the addition of iron. The minimum dose giving stimulation is 0·1 mg. per litre for *Nitrosomonas* and 0·3 mg. per litre for *Nitrobacter*; the optimum dose for both species is about 6 mg. per litre. Larger doses of iron, up to 112 mg. per litre, are tolerated by both kinds of nitrifier (Meiklejohn, 1952 *a*). There is evidence that copper is essential for nitrifiers, but zinc does not appear to be needed (Lees, 1948; Lees and Meiklejohn, 1948). Manganese is toxic to mixed cultures (Meiklejohn, 1952 *a*).

Organic matter and the nitrifiers. In 1899 Winogradsky and Omeliansky published a paper in which they showed that some organic substances, not usually regarded as poisonous, delayed or stopped nitrification in cultures. Owing to the confusion that exists in the minds of some authors between substances which are familiar in the laboratory and those which are common in nature, this work of Winogradsky and Omeliansky has found its way into textbooks in the form of statements such as 'Nitrification does not take place in the presence of organic matter' which is obviously absurd, considering that nitrification goes on actively in manure heaps and sewage-disposal plants, to say nothing of the cowsheds of India.

The substances that Winogradsky and Omeliansky (1899) found to stop nitrification were: in small doses, glucose, peptone, asparagin, and sodium butyrate; in large doses, urine, broth, and sodium acetate. The case of glucose has been re-examined recently; Jensen (1950 *b*) found that his strain of *Nitrosomonas* would tolerate a 10 per cent. solution of glucose sterilized by filtration, but 1·5 to 2·5 per cent. of glucose sterilized by autoclaving stopped nitrification. That is to say, the poisonous substance is not glucose itself, but something formed from glucose by heat; and Winogradsky and Omeliansky sterilized their media by heat. Meiklejohn (1951 *a*) found that 0·33 per cent. glucose sterilized by autoclaving in the medium killed the nitrifying bacteria in mixed cultures; the same dose of glucose sterilized by filtration was harmless to the nitrifiers, but it delayed nitrification in mixed cultures because it encouraged the growth of contaminants.

Peptone is very poisonous to nitrifiers, so much so that media containing peptone are used for a routine test of purity of nitrifying cultures (Gibbs, 1919). Kingma Boltjes (1935) found that the most toxic kinds of

peptone are those with the most free amino-acids; the amino-acid responsible for the toxicity is probably methionine (Quastel and Scholefield, 1949). Sodium butyrate and asparagin have also been shown by recent work to be toxic in small doses (Heubült, 1929; Jensen, 1950 *b*).

But there is no doubt that the natural organic matter of the soil has a favourable rather than an adverse effect on nitrification (Müntz and Lainé, 1907); and Jensen (1950 *b*) has described a strain of *Nitrosomonas* from farm-yard manure that tolerates very high concentrations of sugars and salts or organic acids.

There remains the question whether there may be some kind of organic stimulant or growth factor required by nitrifying bacteria, or whether the old connexion between nitrogenous organic matter and the formation of saltpetre is simply due to the fact that nitrogenous organic matter is a source of ammonia. Murray (1923) and Hes (1937) found that an extract of garden soil had a stimulating effect on nitrification in culture. Fred and Davenport (1921) described the stimulating effect of *Nährstoff-Heyden*, a preparation of egg albumen, on *Nitrobacter*; and Kingma Boltjes (1935) found that *Nährstoff-Heyden* and sodium acetate improved the growth of *Nitrosomonas* and *Nitrobacter*. But these substances were not used as sources of carbon for growth, and their favourable effect may be due to their poising the oxidation-reduction potential of the medium. Meiklejohn (1952 *b*) found that, in mixed cultures, yeast extract, thiamin, and urine had no stimulating effect on nitrification at low concentrations, and delayed or stopped it at higher concentrations. Soil extract had no stimulating effect, nor had *beta*-indoleacetic acid in doses from 0·2 to 50 micrograms in 20 ml.

It is possible that a natural organic stimulant for nitrification exists, but has not yet been found; *Desulphovibric desulfuricans*, a facultative autotroph, grows much better in presence of yeast extract (Butlin, Adams, and Thomas, 1949); and the obligate autotroph *Thiobacillus thiooxidans*, which is known to synthesize a number of growth factors (O'Kane, 1942), produced, under ultra-violet light, a mutant which required yeast extract (Rittenberg and Grady, 1950).

Fat is known to play a very important part in the metabolism of *Thiobacillus thiooxidans* (Umbreit, Vogel, and Vogler, 1942), and it is possible that fat may be important for the nitrifiers too, as Meyerhof (1916) showed that those poisons which were lipoid-soluble had a severe effect on *Nitrosomonas* and *Nitrobacter* in very small doses.

Two Side-tracks in Nitrification

Heterotrophic bacteria which produce small quantities of nitrite from ammonia have been described by several workers. The amounts are very small, of the order of 1 to 2 mg. per litre. Cutler and Mukerji (1931) were careful to exclude nitrate from their medium, so that the nitrite they observed must have been produced by oxidation. An actinomycete producing very small quantities of nitrite from ammonia has recently been described (Isenberg, Schatz, and Hutner, 1952). It has been claimed that the united activities of such organisms account for the nitrification observed in soil; but *Nitrosomonas*, or a related autotrophic

organism, has been found in every soil where it has been seriously looked for, and in which nitrification takes place; and it produces much greater amounts of nitrite than any of the heterotrophs, so the hypothesis seems unlikely.

Pyruvic oxime and oximes of other *alpha*-keto acids are oxidized to nitrite by several species of heterotrophic bacteria that occur in soil (Lees and Quastel, 1946; Jensen, 1951; Quastel, Scholefield, and Stevenson, 1952). Substantial quantities of nitrite are formed, and if oximes are regularly found in soil this process should be important in soil nitrification.

But it still remains true to say that the only bacteria which have been adequately described, and are certainly known to produce nitrite in quantity from ammonia, or to produce nitrate by oxidation of nitrite, are the autotrophic species originally described by Warington and the Franklands, and isolated by Winogradsky.

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[A review of the authors' views on the biochemical aspects of nitrification has been published by Quastel and Scholefield (1951); the reader should not be misled by their use of the words 'Nitrosomonas' and 'Nitrobacter' into thinking that they knew that bacteria of these genera were present in the material they worked with.]

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AN INVESTIGATION OF THE FREE AMINO-ACIDS IN ORGANIC SOIL TYPES USING PAPER PARTITION CHROMATOGRAPHY

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BREMNER (1950) has shown that part of the humus complex consists of amino-acids present in the combined state, though he failed to detect free amino-acids in extracts of the soil samples he investigated. The presence of free amino-acids in soils, though small in amount, would, however, be expected to form a vital link in the breakdown chain from proteinaceous matter to free ammonia, and to be essential in the metabolism of the soil microflora.

The purpose of the present work was to re-examine this question as an approach to the investigation of certain aspects of humus breakdown in natural soils. The soils chosen were mostly organic, taken from under natural vegetation and undisturbed. They cover an extreme range of acidity and of associated humus types.

1. Black, amorphous, greasy, and acid humus layer under knoll oak woodland.
2. Black, amorphous, and acid peat under birch-alder woodland.
3. Dark red-brown, amorphous, and highly oxidized raised-bog peat under subspontaneous pine.
4. Red-brown, partly oxidized raised-bog peat under bog vegetation, much *Calluna* and *Eriophorum vaginatum* (cotton-sedge).
5. Undecayed *Sphagnum* from regenerating bog surface (a reducing material).
6. Brown crumb *mull* soil under oak-ash woodland.
7. Amorphous leaf litter (*mull*) in oak-ash woodland.
8. Undecayed and reducing peat from willow-birch '*carr*'.
9. Black and amorphous fen-peat (calcium saturated). *Phragmites* near.

Samples 3 and 4 represent stages in oxidation of material originally like 5. Sample 4 is from the existing bog surface now partly drained and sample 3 from a site where drainage is more complete so that long-continued oxidation has led to the complete loss of visible plant structure in the peat. All these and sample 8 are from Stribers Moss, north Lancashire. Sample 8 differs in being from the edge of the bog where the peat receives mineral soil drainage. Soils 1 and 6 are from oak woodland on Silurian rock. The former is from a heavily leached and acid knoll soil; sample 6 is from soil flushed by seepage from above.

Samples 1, 2, 6, 7, and 9 are from Roudsea Wood, north Lancashire.

The series of soil samples was collected on the dates shown in Table 1. The samples were transported with the least possible disturbance in air-tight aluminium tins which were placed in cold storage on the following day.

Since fresh soil samples were used it was in all cases possible to express the soil solution using a tincture press. About 50 ml. of each soil solution were generally expressed in this way.

The treatment of the expressed soil solutions prior to their application to paper chromatograms was as follows: each soil solution was first centrifuged at 1,000*g* for 30 minutes to remove suspended matter and then evaporated to about 2–3 ml. *in vacuo* over conc. H_2SO_4 at laboratory temperature. The concentrated extract was then desalted if necessary (Consden, Gordon, and Martin, 1947), again centrifuged, and finally evaporated to dryness *in vacuo* as before.

Chromatographic technique. The residue from each soil solution was redissolved in a known small volume of distilled water (0·5 ml.) and then a volume equivalent to 5 ml. of the original soil solution was applied as a small spot (1 cm. in diameter) near one corner of a large sheet (22½ in. × 18½ in.) of Whatman No. 4 filter-paper. The chromatograms prepared in this way were developed as described by Fowden (1951), using water-saturated phenol in an ammonia atmosphere as the first solvent and the *n*-butanol-acetic acid mixture of Partridge (1948) as the second solvent. After drying the chromatograms, the final positions of the amino-acids present were revealed by spraying with a 0·1 per cent. solution of ninhydrin in water-saturated *n*-butanol followed by a short heating period at 90° C.

Results

As shown in Table 1, free amino-acids were found in all the soils examined. In undecomposed *Sphagnum* litters and in the base-saturated fen peat only faint traces of a few amino-acids were found to be present. Aspartic and glutamic acids, alanine, glycine, and serine were found to be most widely distributed. It will be noted that proline, tyrosine, cystine, methionine were not found and the amides, asparagine, and glutamine were only once detected. The total concentration of the amino-acids present in the samples collected in February 1951 and April 1952 was considerably greater than in those collected in July 1951.

Discussion and Summary

Whilst free amino-acids have definitely been detected in the organic soils studied, the amounts are small. The total concentrations given in the table are estimates obtained from ordinary qualitative chromatograms, and therefore are probably subject to an error of ±50 per cent. The results obtained suggest that there may be a seasonal difference in the total number and concentration of free amino-acids, and that an inverse relationship may exist between soil pH and the total concentration of free amino-acids in the soil solution.

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TABLE 1

Free Amino-acids in Soil Types

Soil type No.	1	2		3		4		5	6	7	8	9	
Date sampled	4/52	2/51	7/51	2/51	7/51	2/51	7/51	2/51	4/52	7/51	7/51	2/51	7/51
pH	3·0	3·3	3·2	3·4	3·0	3·9	4·0	4·0	4·35	5·1	5·3	6·7	6·6
Serine	+++	+++	++	++	++	++	+	++	+	+	+	−	+
Glycine	+++	++	+	++	++	++	+	++	−	+	+	−	+
Alanine	++++	++++	++	++	++	++	+	++	+	+	+	−	+
Aspartic acid	+++	+++	+	−	+	++	−	−	+	+	−	+	−
Glutamic acid	+++	+++	++	−	+	++	−	−	++	+	−	++	−
Threonine	+	++	−	−	+	++	−	−	−	−	−	−	−
Leucines	++	++++	−	−	−	++	−	−	−	−	−	−	−
Valine	+	+++	+	−	+	−	−	−	−	−	−	−	−
β-Alanine	−	++	−	−	−	−	−	−	−	−	−	−	−
Basic amino-acids	−	++	−	−	+	−	−	−	−	−	−	+	−
γ-NH_2-butyric acid	++	−	−	−	−	++	−	−	−	−	−	−	−
Asparagine	+	−	−	−	−	−	−	−	−	−	−	−	−
Glutamine	+	−	−	−	−	−	−	−	−	−	−	−	−
Total estimated μg.–NH_2–N/5 ml. soil soln.	24	25	6	6	10	15	2	6	5	3	2	4	2
Water content (% dry wt.)	275	430	400	1,050	1,070	1,110	1,110	5,300	73	140	1,830	480	460
Loss on ignition (% dry wt.)	84	90	88	98	97	96	97	96	16	54	93	56	60
Total N content (% dry wt.)	2·39	1·38	—	1·10	—	1·80	—	1·58	0·775	1·45	2·43	2·32	—

Approximate value of symbols:

\+ trace
++ 2μ gms. –NH_2–N
+++ 3μ gms. ,,
++++ 4μ gms. ,,
− none detected

THE EFFECT OF EXCHANGEABLE CATIONS ON THE RETENTION OF PHOSPHATE BY CLAY

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Introduction

Of the many reactions that have been proposed to account for the retention of phosphate by soil one is that phosphate can be adsorbed by clay through the intermediary of exchangeable calcium ions. It was first put forward by Demolon and Barbier (1930). They had observed that a soil clay sorbed less phosphate when acid than when saturated with calcium ions, even where precipitation of an insoluble calcium phosphate was precluded by a low pH value and low concentrations of calcium and phosphate ions. More satisfactory experiments were later carried out by Demolon and Bastisse (1934), by Barbier, Chabannes, and Miallet (1946), and by Barbier and Chabannes (1949). They found that acid clays titrated with calcium hydroxide sorbed appreciably more phosphate than when titrated with potassium hydroxide to the same pH value. This difference was found not only with a soil clay but with kaolinite and montmorillonoid clay minerals. Similar experiments were carried out by Scarseth (1935) and Allison (1943), who drew the same conclusion: that the exchangeable calcium ions can act as bridges between phosphate ions and the clay surface. Recently Birch (1951) has used this hypothesis to explain the high availability of phosphate in East African soils well supplied with calcium.

The hypothesis seems unlikely to be true unless a complex cation such as $[Ca(H_2PO_4)]^+$ is formed, and no evidence for this seems to exist. Further, in the experiments referred to above, the monovalent cation itself sometimes caused a small increase in phosphate retention when the clay was titrated up to pH 6. This was especially noticeable with clays low in free sesquioxides. The monovalent and divalent cations may thus differ only quantitatively in their effect on phosphate retention, but the explanation that the exchangeable cation acts as a bridge between the phosphate ion and clay is untenable with the monovalent cations. Experimental evidence will therefore be presented to support an alternative explanation.

Experimental Methods

Retention of phosphate was measured with the following clays:

1. $< 1{\cdot}4\mu$ kaolinite containing no impurities detectable by X-ray diffraction and having the theoretical chemical composition of a pure sample.
2. $1{\cdot}4$–$0{\cdot}13\mu$ montmorillonoid containing no impurities detectable by X-ray diffraction.

3. Rothamsted subsoil clay containing partially hydrated illite as the chief constituent, a small percentage of kaolinite, free iron oxide probably as goethite and possibly aluminium oxide. It was used in two forms: (*a*) as $< 1{\cdot}4\mu$ clay fraction; (*b*) as unfractionated subsoil containing 49 per cent. $< 2\mu$ clay.

Before separating the $< 1{\cdot}4\mu$ Rothamsted clay fraction the subsoil was oxidized with hydrogen peroxide and the suspension was made 0·2 N with respect to hydrochloric acid. After separation, all the clays were washed with 0·005 N hydrochloric acid to convert them into acid clays. Excess acid was washed out and the samples were dried at 40° C., crushed, sieved through a 40 I.M.M. sieve, and stored in a desiccator.

The unfractionated Rothamsted subsoil was prepared by leaching with 0·5 N acetic acid until free from exchangeable bases and then with distilled water to remove excess acid. The sample was dried, lightly crushed, and sieved as for the clays. The small amount of coarse sand that was retained on the sieve (about 2 per cent. of the total subsoil) was rejected.

The treatment with hydrochloric acid in the separation of the Rothamsted clay is rather drastic and might have affected the surface structure of the clay, though no alteration could be detected by X-ray analysis. A check on the effect of the N/2 acetic acid on the Rothamsted subsoil was made by comparing the subsequent phosphate retaining properties with those of a sample leached with N/100 hydrochloric acid. No difference was found.

The technique of measuring phosphate retention was as follows.

Samples of 0·2 g. clay or subsoil (0·1 g. in the case of Rothamsted clay) were weighed into 50-ml. tubes. Enough CO_2-free distilled water was added to each to give a final volume of 44 ml. Acid or alkali was added to adjust the pH value in the range 1–10, and lastly dilute phosphoric acid to give an initial concentration of approximately $2{\cdot}3 \times 10^{-4}$ moles H_3PO_4 per litre. The tubes were shaken for 24 hours at 20° C. Samples of about 4 ml. of the suspension were taken for the determination of pH using a glass electrode and a calomel saturated potassium chloride standard half-cell. In some of the experiments the samples were made 0·02 N with respect to calcium chloride by the addition of 0·1 ml. of a 0·8 N solution. The bulk of the suspension was centrifuged, and if the resultant supernatant liquid was cloudy it was ultrafiltered by the technique described previously (Wild, 1950). The clear solutions were analysed for phosphate by the molybdenum blue method of Truog and Meyer (1929). After subtracting the corresponding 'blank 'values when these occurred, the differences between the amounts of phosphate found in solution and that added initially were calculated as millimoles H_3PO_4 retained per 100 g. oven-dry subsoil or clay.

Experimental Results

In Figs. 1 to 3 are summarized the results of the retention of phosphate by Rothamsted clay, kaolinite, and the montmorillonoid. It should be noted that the pH values of the Rothamsted clay were determined in

aqueous suspension whereas those of the kaolinite and the montmorillonoid were in 0·02 N calcium chloride. With the two clay minerals the

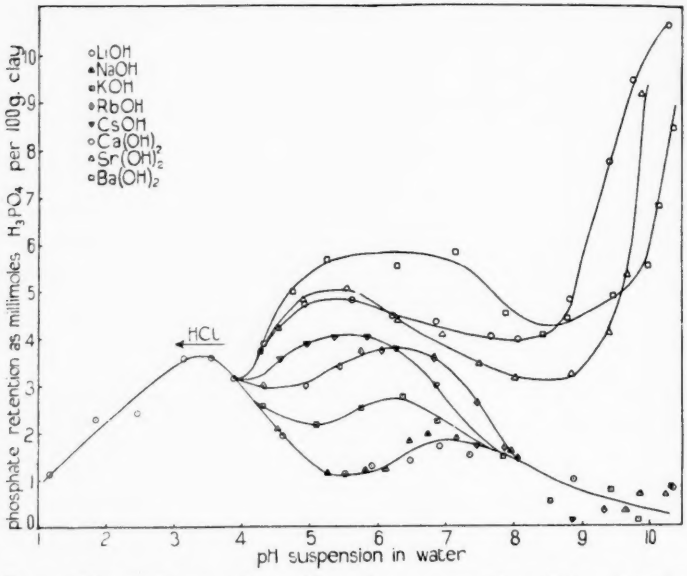

FIG. 1. Effect of the exchangeable cation on retention of phosphate by Rothamsted clay. Phosphate addition: 10·6 millimoles H_3PO_4 per 100 g. clay.

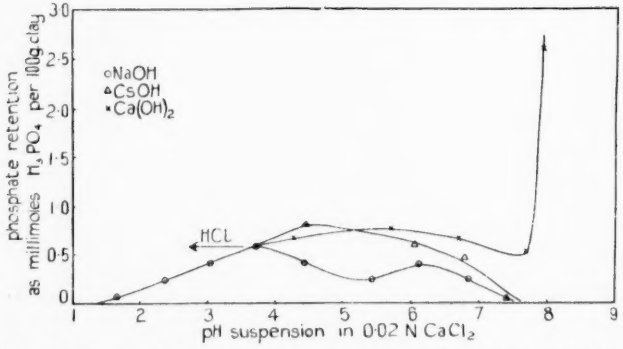

FIG. 2. Effect of the exchangeable cation on retention of phosphate by kaolinite. Phosphate addition: 5·1 millimoles H_3PO_4 per 100 g. clay.

only alkalis used were sodium, caesium, and calcium hydroxides, but the Rothamsted clay was titrated with all the available group 1 A and 2 A metal hydroxides except magnesium hydroxide which gave a solution too weak to change the pH by more than a very small amount.

There was no 'blank' with the montmorillonoid, and 'blank' values could be detected with the kaolinite only outside the pH range 2·0–7·5 where they were still very small. With the Rothamsted clay the 'blank' values were much greater. About 0·5 millimole H_3PO_4 was dissolved per 100 g. clay at pH 2 and about 2·2 millimoles at pH 9 in the presence of the group 1 A metal hydroxides. In Fig. 1 the 'blank' values with each alkali at the corresponding pH values have therefore been subtracted.

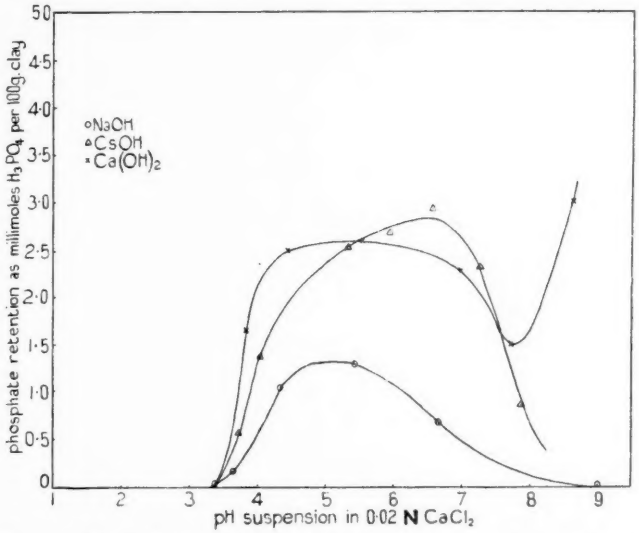

FIG. 3. Effect of the exchangeable cation on retention of phosphate by a montmorillonoid. Phosphate addition: 5·3 millimoles H_3PO_4 per 100 g. clay.

All three clays show much greater retention of phosphate in the presence of caesium and calcium ions than in the presence of sodium. These ions will, after titration of the acid clays, be present mainly as exchangeable cations. With the Rothamsted clay at pH 5·5 the effect of the exchangeable cations is in the order Li = Na < K < Rb < Cs < Ca < Sr < Ba. Above pH 9·5 the order with the group 2 A metals is reversed, most phosphate being retained by the calcium clay, and least by the barium clay. As this is the order of insolubility of the corresponding phosphates, precipitation of phosphate is indicated.

At low pH values, for example at pH 5·5 with the Rothamsted clay, direct precipitation by the metal of the added alkali is improbable since the solubility products of the corresponding phosphates are not exceeded. With the monovalant ions the bridging mechanism seems untenable and another theory must therefore be examined.

This is that the exchangeable cations have an indirect effect: that they influence the extent to which aluminium and possibly iron present in the clay react with phosphate. In the kaolinite and the montmorillonoid

the amount of iron present is very small and must have a negligible effect on phosphate retention. In order to determine the relative importance of iron and aluminium in the Rothamsted subsoil, the effect of the exchangeable cation on phosphate retention was investigated after the

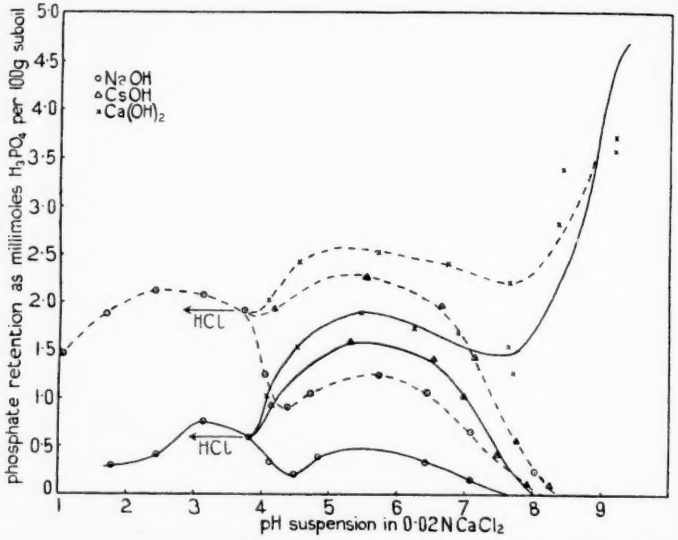

FIG. 4. Effect of the exchangeable cation on retention of phosphate by Rothamsted subsoil after Na hydrosulphite treatment. Full lines—treated sample, broken lines—no hydrosulphite treatment. Phosphate addition: 5·2 millimoles H_3PO_4 per 100 g. subsoil.

free sesquioxides had been removed. Free iron oxide was removed from the subsoil by the sodium hydrosulphite method of Galabutskaya and Govorova as described by Deb (1950). Total sesquioxides were dissolved with acid ammonium oxalate in sunlight, which Schofield (1949)

TABLE 1

Effect of Treatment to remove Iron and Aluminium from Rothamsted Subsoil

	Percentage of subsoil dissolved		*Titration to pH 6·0 in aqueous suspension. m.e. alkali/100 g.*
	Fe	Al	
No treatment . . .	. .	. .	19·5
Acid ammonium oxalate .	3·8	1·1	8·5
Na hydrosulphite 1 hr. .	3·5	0·26	19·5

found effective for removing the source of positive charges in the Rothamsted subsoil clay. The amounts of iron and aluminium dissolved were determined colorimetrically, and the results are recorded in Table 1.

The treated subsoil samples were leached with 0·5 N acetic acid, dried and crushed, and the retention of phosphate was determined as

described previously. The results for the subsoil treated with sodium hydrosulphite are shown in Fig. 4 and those for the subsoil treated with acid ammonium oxalate in Fig. 5. Each figure includes, for comparison, corresponding phosphate retention results for the untreated subsoil.

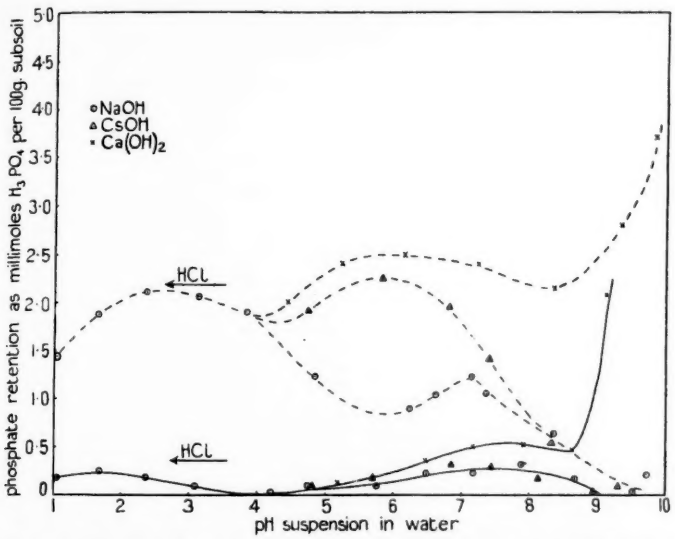

FIG. 5. Effect of the exchangeable cation on retention of phosphate by Rothamsted subsoil after acid ammonium oxalate treatment. Full lines—treated sample, broken lines—no oxalate treatment. Phosphate addition: 5·2 millimoles H_3PO_4 per 100 g. subsoil.

The differences in phosphate retention by the subsoil titrated with sodium, caesium, and calcium hydroxides have remained unaffected by the sodium hydrosulphite treatment, but have practically disappeared after treatment with acid ammonium oxalate. Thus removal of free iron oxide does not alter the magnitude of the exchangeable cation effect but vigorous removal of aluminium does. It therefore seems that if the exchangeable cations influence the extent to which a constituent of clay reacts with phosphate, this constituent must be aluminium. The reactivity of iron is not influenced by the exchangeable cation.

The evidence from this experiment is not wholly satisfactory, however, because the sodium hydrosulphite has not removed all the iron oxide, and it has dissolved some aluminium. Also, the titration curves indicate that the treatment with acid ammonium oxalate followed by 0·5 N acetic acid has, at least partially, destroyed the clay structure. The amounts of calcium hydroxide needed to titrate the subsoil samples to pH 6·0 in aqueous suspension are given in Table 1. An attempt was made to extract all the iron oxide with sodium hydrosulphite by extending the extraction time, but the titration curve was again appreciably changed.

In the method used for measuring phosphate retention, alkali and dilute phosphoric acid were added together to the acid clay. The effect of the alkali is to precipitate the exchangeable aluminium ions as

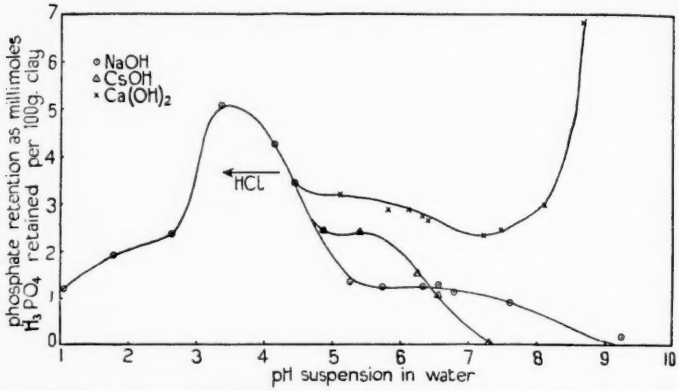

FIG. 6. Effect of the exchangeable cation on retention of phosphate by Rothamsted clay after shaking 28 days with alkali. Phosphate addition: 10·6 millimoles H_3PO_4 per 100 g. clay.

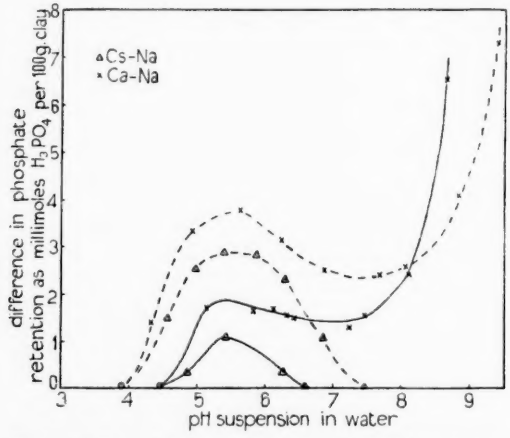

FIG. 7. Effect of 28 days' shaking with alkali on retention of phosphate by Rothamsted clay. Full lines—differences from Fig. 6, broken lines—differences from Fig. 1.

aluminium hydroxide and at the same time the phosphate may react to form a basic compound such as $Al(OH)_2H_2PO_4$. The rate of formation of such a basic compound should be reduced if the aluminium is brought to equilibrium with the alkali before the phosphate is added. The three experiments that follow were designed to investigate this point.

Samples of 0·1 g. of the Rothamsted clay were shaken for 28 days at 25° C. with water and with the necessary acid or alkali to adjust the pH value. Dilute phosphoric acid was added and the retention of phosphate during 24-hour shaking periods was determined in the usual way. The results are shown in Fig. 6. To facilitate comparison between these

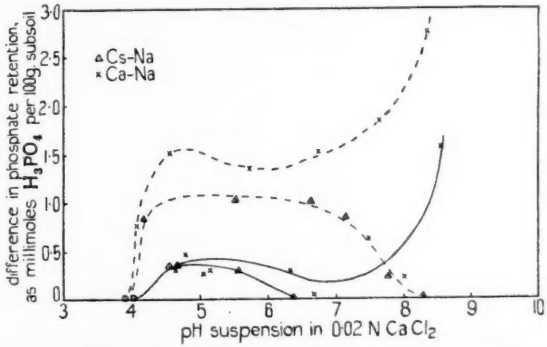

FIG. 8. Effect of refluxing with alkali on retention of phosphate at 25° C. by Rothamsted subsoil. Full lines—refluxed, broken lines—not refluxed. Phosphate addition: 5·2 millimoles H_3PO_4 per 100 g. subsoil.

results and the corresponding ones in Fig. 1 in which the phosphate and alkali were added together, the differences between the sodium and caesium, and the sodium and calcium systems, are shown for both treatments in Fig. 7.

The differences are reduced by the 28-day treatment with alkali but still remain appreciable. It is concluded either that precipitation of the aluminium hydroxide is incomplete even in 28 days, which seems unlikely except where there is insufficiency of alkali, or that the phosphate is still able to react with the aluminium, perhaps by displacing hydroxyl ions.

In an attempt further to reduce the difference in phosphate retention between the calcium and caesium clays on the one hand, and the sodium clay on the other, a more drastic treatment with alkali was carried out, this time by boiling the Rothamsted subsoil under reflux for 24 hours.

Samples of 0·2 g. of subsoil were suspended in sufficient water and alkali to give a volume of 42 ml. and a pH value in the range 4·0–8·5. After 24 hours' heating the flasks were cooled, distilled water was added to make up the evaporation loss, and the retention of phosphate during 24 hours' shaking at 25° C. was determined in the usual way. Fig. 8 shows that the differences in phosphate retention between the calcium, caesium, and sodium clays are again reduced, but not eliminated.

These results can be explained by a decrease in the rate of reaction between aluminium and phosphate. The next experiment was carried out to investigate whether this rate of reaction could be increased by heating the clay and phosphate solution for 24 hours at 100° C.

Samples of Rothamsted subsoil were heated under reflux with alkali for 24 hours as described in the last experiment. Dilute phosphoric acid was added and the retention of phosphate during a further period of 24 hours' heating under reflux was determined. Fig. 9 shows that the differences in phosphate retention between the calcium, caesium, and sodium clays are slightly increased when the phosphate reacts at 100° C.

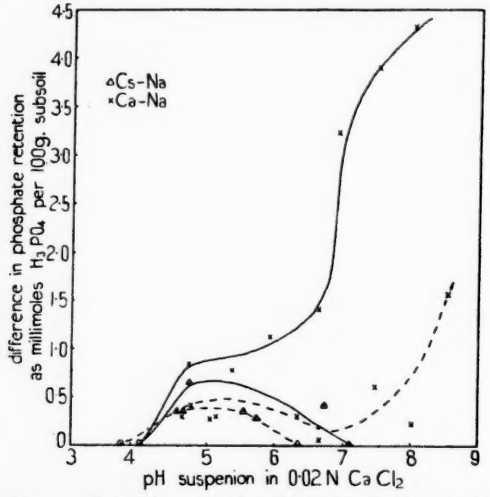

FIG. 9. Retention of phosphate by Rothamsted subsoil after refluxing with alkali. Full lines—phosphate retention at 100° C., broken lines—retention at 25° C. from Fig. 8. Phosphate addition: 5·2 millimoles H_3PO_4 per 100 g. subsoil.

Above pH 6 with the calcium clay retention has been considerably increased.

These three experiments are inexplicable on the theory that calcium ions act as intermediaries between phosphate ions and clay unless the calcium ions are 'fixed' within the clay structure as a result of the more extreme experimental conditions. From the titration curves such fixation seems unlikely.

The amounts of alkali required to titrate the subsoil to pH 6 in the presence of 0·02 N calcium chloride are given in Table 2. The data refer to sodium and calcium hydroxides. In aqueous suspension the titration curves of the subsoil samples heated under reflux were similar to those given in Fig. 12 for the unheated subsoil, except that above pH 6 the caesium and calcium hydroxide curves almost coincided.

It is therefore probable that heating with alkali causes no 'fixation' of calcium ions and does not affect the amount of exchangeable aluminium displaced. It only 'ages' the aluminium hydroxide.

Having shown that the exchangeable cation influences phosphate retention only by affecting the reaction between phosphate and the aluminium in clay, experiments were carried out to investigate whether the same effect occurs in dilute solutions of an aluminium salt, and with an organic exchange resin.

TABLE 2

Effect of heating with Alkali on Titration of Acid Subsoil to pH 6·0

Pretreatment with alkali	*Temperature of phosphate retention*	*Titration to pH 6·0 m.e. alkali/100 g.*
None	25° C.	22·0
24 hours at 100° C. . . .	25° C.	24·0
24 hours at 100° C. . . .	100° C.	22·0

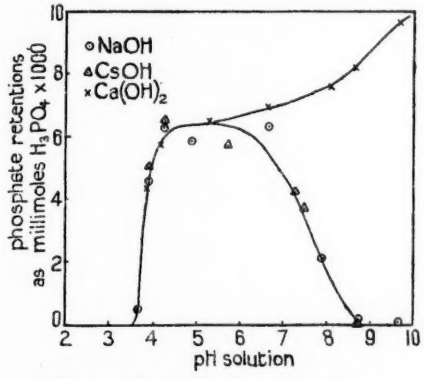

FIG. 10. Precipitation of phosphate by aluminium sulphate solution.

Aliquots of a dilute solution of aluminium sulphate containing 0·36 mg. Al were pipetted into tubes. This amount of aluminium corresponds with the exchange capacity of 0·1 g. of Rothamsted clay. Distilled water to give a final volume of 44 ml. was added followed by sodium, caesium, or calcium hydroxides to adjust the pH value, and finally dilute phosphoric acid. The tubes were shaken at 25° C. for 24 hours and the pH values and the phosphate contents of the solutions were determined. Duplicates were more variable than with clay. Average values for the amounts of phosphate retained by the precipitate are shown in Fig. 10. Precipitation of phosphate is the same with sodium hydroxide as with caesium hydroxide, and it is only above about pH 6 that there is greater precipitation with calcium hydroxide. Apart from calcium hydroxide above pH 6, therefore, the precipitation of phosphate is independent of the kind of alkali present.

The results with the organic exchange resin are given in Fig. 11. The experiments were done with aluminium and hydrogen saturated forms of Zeo-Karb 315, which is a sulphonated resin supplied by the Permutit

Company. They were made by leaching with aluminium chloride and hydrochloric acid solutions respectively, and then with distilled water.

Samples of 0·1 g. of dry resin were titrated with alkali in the presence of dilute phosphoric acid and the retention of phosphate was determined after 24 hours' shaking at 25° C.

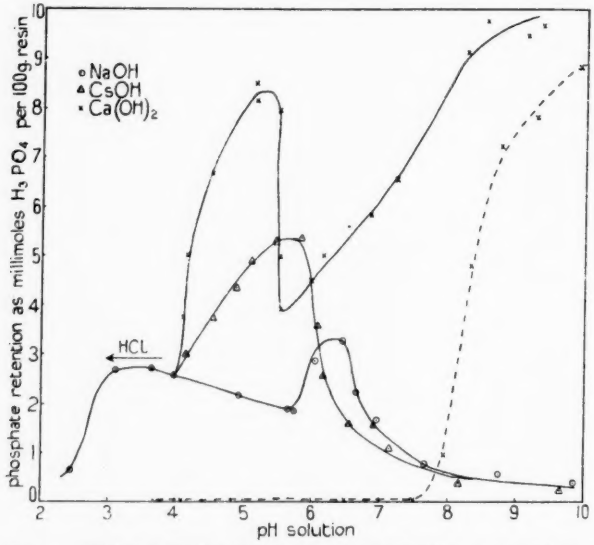

FIG. 11. Effect of exchangeable cation on retention of phosphate by exchange resins. Full lines—aluminium resin, broken lines —hydrogen resin. Phosphate addition: 10·3 millimoles H_3PO_4 per 100 g. resin.

From the results in Fig. 11 it will be seen that, as with clays, the aluminium resin showed greater retention of phosphate when titrated with calcium hydroxide and least when titrated with sodium hydroxide. The curves differ from those with clay in that the peaks of phosphate retention are narrower, and also occur at different pH values.

Below pH 7·5 the hydrogen resin titrated with calcium hydroxide retained no phosphate. At higher pH values a precipitate, which was presumably some form of calcium phosphate, could be observed in the tubes. Since the aluminium resin showed a peak in phosphate retention at about pH 5 when titrated with calcium hydroxide whereas the hydrogen resin did not, it follows that this peak, and in fact all retention of phosphate below pH 7·5, must be attributed to the presence of aluminium. The evidence from the hydrogen and aluminium resins therefore supports the previous evidence with clays, that the exchangeable cations influence phosphate retention only by affecting the reaction between aluminium and phosphate.

Discussion

Having established that the exchangeable cations affect the reaction between phosphate and aluminium, some possible explanations of the effect can now be advanced.

Swenson, Cole, and Sieling (1949) showed that when a solution of an aluminium salt is titrated with alkali in the presence of excess phosphate the basic aluminium phosphate $Al(OH)_2H_2PO_4$ is precipitated. The aluminium in the present experiments with acid clays is present in exchangeable form and titration of these acid clays is, according to Schofield (1949), essentially the precipitation of the exchangeable aluminium as aluminium hydroxide. Since the titration was done in the presence of phosphate, $Al(OH)_2H_2PO_4$ or a more basic phosphate is probably formed. The difference in the retention of phosphate by clays and the aluminium resin according to the nature of the exchangeable cation must therefore be due to the extent of formation of this basic aluminium phosphate. Two possible explanations for this will be considered.

The first is suggested by the titration curves. The amounts of alkali required to increase the pH value varied with the kind of alkali used. With the three alkalis most commonly used the order was calcium hydroxide > caesium hydroxide > sodium hydroxide, which is the same order as for phosphate retention. If it can be assumed that the amounts of alkali used correspond to the release of equivalent amounts of aluminium, the effect of the exchangeable cation on phosphate retention may be explained by different amounts of aluminium being exchanged. If this is the case there should be a constant ratio (theoretically 1:1) between the number of milli-equivalents of alkali added (and hence of aluminium exchanged) and the number of milli-equivalents of phosphate retained. This ratio is difficult to calculate with clays because of the uncertainty in interpreting the pH values of deflocculated clays, but with the aluminium resin this difficulty does not arise. The ratios with the aluminium resin at three pH values are given in Table 3.

TABLE 3

	Sodium hydroxide			*Caesium hydroxide*			*Calcium hydroxide*		
pH	*m.e.* OH' *added*	*m.e.* H_2PO_4' *sorbed*	*Ratio*	*m.e.* OH' *added*	*m.e.* H_2PO_4' *sorbed*	*Ratio*	*m.e.* OH' *added*	*m.e.* H_2PO_4' *sorbed*	*Ratio*
4·5	7	2·3	3·0	13	3·6	3·6	25	6·7	3·7
5·0	12	2·0	6·0	23	4·6	5·0	41	8·2	5·0
5·5	21	1·9	11·1	37	5·3	7·0	70	*	..

* As will be seen in Fig. 12 no accurate value can be given.

The ratios are always greater than 1. Since only 10·3 millimoles H_3PO_4 were added per 100 g. resin, high ratios must occur for more than equivalent additions of alkali. Nevertheless one would expect, especially at pH 4·5, a much narrower ratio from that found, though it is worth

noting that at both pH 4·5 and 5·0 the ratios are of the same order for the three alkalis.

The second possible explanation that will be considered is that the exchangeable cation affects the distribution of phosphate ions in the Gouy layer and it is this which determines the amount of phosphate sorption. All the clays used in the present experiments have a net

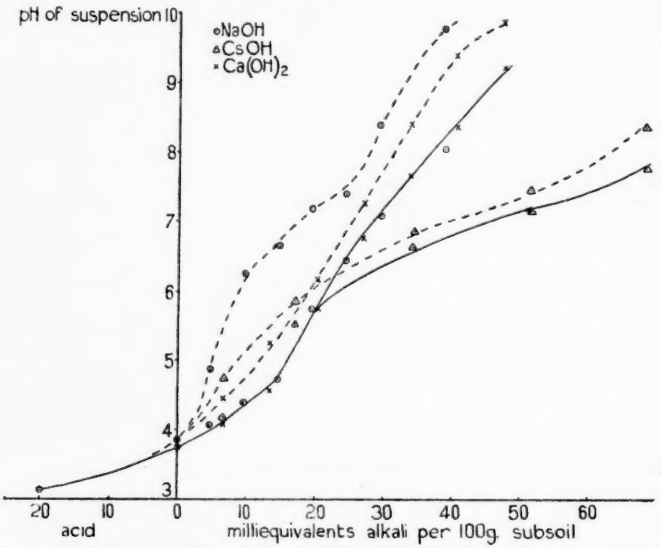

FIG. 12. Potentiometric titration of Rothamsted subsoil in presence of 5·2 millimoles H_3PO_4 per 100 g. Full lines—suspension in 0·02 N $CaCl_2$, broken lines—suspension in water.

negative charge and the concentration of phosphate ions in the Gouy layer will be less than in the outside solution. The actual concentration will depend on the zeta-potential.

It is known that the zeta-potential of a clay is greatest when lithium is the exchangeable cation and it decreases as the size of the hydrated cation decreases and its charge increases. It is reasonable to expect that the phosphate concentration in the innermost part of the Gouy layer will be in the reverse order, that is, with the group 1 A metals will be least with lithium and greatest with caesium. The amount of aluminium phosphate formed will then be determined by the concentration of phosphate.

The two hypotheses that have been put forward lead to the same result. Which is correct cannot be determined from the present experiments.

One feature of the present experiments is that in the aluminium-containing systems studied precipitation of phosphate in the presence of calcium, apart from that as aluminium phosphate, occurred at anomalously low pH values. Calculations from the known solubility

products show that under the conditions of the present experiments precipitation of any calcium phosphate is improbable below pH 7, with some uncertainty about hydroxlapatite. It was, however, found that on titration with calcium hydroxide retention of phosphate increased progressively above pH 5·5–6·5 with solutions of aluminium sulphate (see Fig. 10), above pH 5·5 with the aluminium resin (see Fig. 11), and above pH 6·5 with the Rothamsted subsoil at 100° C. (see Fig. 9).

The explanation is uncertain. There might be either adsorption on to the surface of the solid phase or the formation of a complex calcium aluminium phosphate, such phosphates being listed by Hey (1950).

Summary

The theory that exchangeable cations act as intermediaries between phosphate and clay is considered improbable. It is alternatively suggested that the exchangeable cations determine the extent of formation of basic aluminium phosphate. The evidence is as follows:

1. The exchangeable cation effect is found with monovalent as well as with divalent ions.
2. The effect is reduced when the clay is equilibrated with the alkali before adding the phosphate, but is increased if the treatment with phosphate is subsequently done at a high temperature.
3. The effect is found with an aluminium resin but not with a hydrogen resin or with aluminium sulphate solutions.

It is less certain how the formation of the aluminium phosphate comes to be affected by the exchangeable cation. There are two possible causes, both of which might apply:

1. That the cations determine the amount of reactive aluminium.
2. That the cations determine the distribution of phosphate ions within the Gouy layer.

Acknowledgement

The author wishes to express his indebtedness to Dr. R. K. Schofield for his helpful criticism of certain parts of this work.

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PHOSPHATE MOVEMENT AND NATURAL DRAINAGE

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MANY studies of phosphate fixation in soils have been made and reviewed (Wild, 1950). There appears to be a consensus of opinion that when a plant-available phosphate such as superphosphate has been applied on or near the surface of soil, the phosphate remains mostly within, or but little below, the zone of application; i.e. that the downward movement, in particular, of applied phosphate is slow and much restricted. A restriction on movement of initially soluble or available phosphate may be imposed by one or more of the phenomena indistinctly known as fixation.

Workers on fixation and on the movement of phosphate in soils appear to have tended to correlate the two phenomena and to relate both to degree of acidity, with secondary regard to other factors such as organic matter and the presence of free calcium carbonate. An outstanding paper on the effect of varying degrees of acidity upon fixation is that of Gaarder (1930).

The purpose of this paper is not to discuss in detail the mechanisms of phosphate fixation, but to give experimental evidence about the varying rates and degrees of movement of the phosphate of superphosphate after that fertilizer had been applied on the surface of undisturbed leys maintained on soils of differing character and having differing modes of natural drainage. No similar previous study is known to have been published. The only comparable studies are those of Glentworth (1947) and Glentworth and Dion (1949), who investigated the distribution of phosphate—presumably partly natural and partly the residue of fertilizer applied in the ordinary course of farming—in arable soils of different degrees of natural drainage.

Other studies immediately relevant to this paper are those of Stephenson and Chapman (1931), Robinson and Jones (1927), and Doak (1933, 1942). Stephenson and Chapman found an appreciable penetration of phosphate below the surface foot in light- and medium-textured soils. Their results indicated that more rapid penetration of phosphate was effected through a few heavy applications of phosphate than through more numerous, lighter doses. Robinson and Jones, unlike most other workers, found that phosphate (as basic slag) applied to rough grazings was rapidly leached. For soils of north Wales, these workers suggested a division of soil phosphate into two groups: (*a*) the natural phosphorus compounds which are subject to negligible wastage by leaching, and (*b*) the unstable phosphorus compounds of added dressings which are removed fairly rapidly from the surface layers by percolating waters. Doak showed that during the 8 years of a trial on penetration of phosphate applied to cultivated grassland in New Zealand, the movement of phosphate into the 6-in. and 10-in. layers of soil was quite appreciable. His

results supported the division of soil phosphate as postulated by Robinson and Jones.

Experimental

To study the movement of fertilizer phosphates, an experiment was carried out on a farm at Killearn, Stirlingshire. The experimental treatment consisted of a single uniform application of superphosphate, supplying P_2O_5 at the rate of 240 lb. per acre, on five plots of grassland each $\frac{1}{40}$ acre in area. The plots, numbered 1, 3, 5, 7, 9, were each accompanied by a control plot numbered respectively 2, 4, 6, 8, 10, to which no phosphate was applied experimentally. All plots were unfenced and continued to be grazed by cattle and sheep in the ordinary course of husbandry. No fertilizer was otherwise applied to any of the plots.

The soil types were as follows:

Plots 1, 2. Old Red Sandstone boulder clay; poorly drained; pH about 6·5.
Plots 3, 4. Old Red Sandstone boulder clay; freely drained; pH about 6·5.
Plots 5, 6. Old Red Sandstone boulder clay; freely drained; pH about 5·3.
Plots 7, 8. Littoral sands; slightly poorly drained; pH about 6.
Plots 9, 10. Littoral sands; poorly drained; pH about 6.

Superphosphate was applied in June 1947, when the grass leys were about 4 years old. The rainfall in the area is approximately 39 in. per annum; average annual temperature 48° F.

Samples of soil were taken to a depth of 7 in. with the aid of a specially designed borer. Samples were taken from each plot immediately before the superphosphate was applied and at intervals thereafter for 3 years. Each of the 7 in. of soil from each sampling was analysed for total phosphate by the method of McGregor (1950) which is based on digesting the soil with concentrated sulphuric and nitric acids; and for available or readily soluble phosphate by the method of Williams and Stewart (1941) based on extraction with 0·5 N acetic acid. Some results are given in graphic form in Fig. 1.

No additional fertilizer or other experimental treatment was given during the 3 years, so the results can be taken as being effects derived essentially from the superphosphate added in 1947, though the initial condition of the soil was modified by unknown earlier treatment in the ordinary course of husbandry, and the retention and movement of phosphate was modified during the experiment by the actions of the grazing animals, which were not controlled by the experimenter. It is felt that these conditions were fair and necessary, in the sense that to depart from them would render the experiment unduly artificial and thus rob it of much of its purpose and practicality.

Results

I. *Available phosphate*

(*a*) *Old Red Sandstone boulder clay* (plots 1, 2, 3, 4, 5, 6). On this soil comparisons were made of: (i) an area which has good natural drainage conditions (plots 3 and 4) and one where there is impeded drainage (plots 1 and 2); (ii) two areas of good natural drainage but

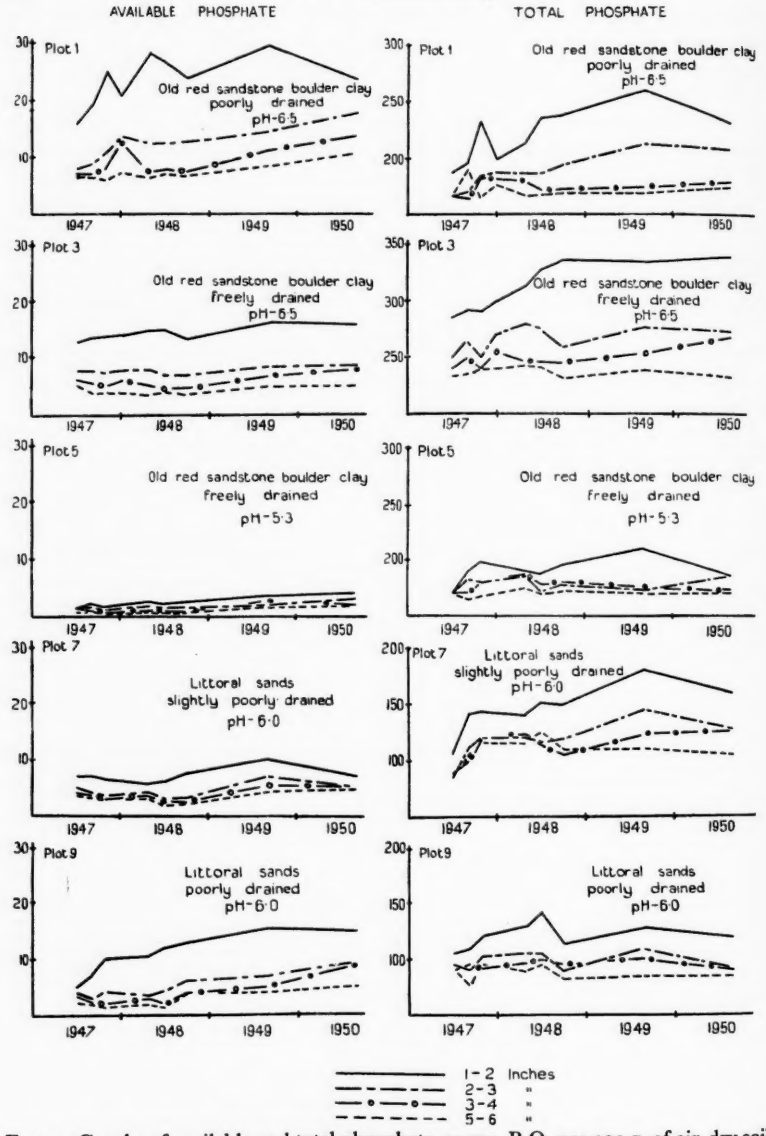

FIG. 1. Graphs of available and total phosphate, as mg. P_2O_5 per 100 g. of air-dry soil, at four selected depths in each phosphate-treated plot, 1947–50.

differing in soil reaction. In plots 3 and 4 the pH is near 7, and in plots 5 and 6 the pH is about 5·3.

Plots 1 and 2 were below plots 3 and 4 in the same field, which was a slope with north aspect.

Analyses of original available-phosphate status of these plots showed that before treatment the percentage of readily soluble ('available') phosphate was highest in the poorly drained neutral associate and lowest in the acid freely drained.

The available phosphate of the control plots remained remarkably constant throughout the period of the experiment, so that they preserved the ranking order just mentioned.

The effect of the superphosphate dressing on the available phosphate in the soil was most marked in the 1-in. and 2-in. layers of all plots (1, 3, 5). There was sometimes an indication of penetration of soluble phosphate to greater depths, but this movement, where it existed, appeared to be very slow.

A comparison of the percentages of available phosphate in the various layers of plots 1, 3, and 5 shows that treatment with superphosphate led to a larger increase of available phosphate in the top 3–4 in. of plot 1 than near the surface of plots 3 and 5.

The results also indicate that in plot 1 (the poorly drained soil) treatment tended to increase the available phosphate down to depths of 6–7 in. In plot 3 (the freely drained soil) treatment produced no significant rise in the percentage of available phosphate below depths of 3–4 in. The freely drained, more acid soil of plot 5 showed even less effect.

In plot 1, which showed the greatest penetration of available phosphate into soil of this type, it was only after 2 years that there was any significant rise in the percentage of available phosphate in the 4-in. layer.

(*b*) *Littoral sands* (plots 7, 8, 9, 10). On this soil type a comparison was made between a slightly poorly drained area (plots 7 and 8) and the poorly drained plots 9 and 10.

The results on this soil were very similar to those on the boulder clay. Again it was found that the effect of superphosphate dressing in increasing the available phosphate mainly affected the top 2-in. layer of soil. The available phosphate of control plots, as in the control plots of Old Red Sandstone boulder clay, remained remarkably constant throughout the period of the experiment.

The rise in available-phosphate content was more marked in the wetter soil, wherein, under these poor drainage conditions, there was a significant rise in the percentage of available phosphate at a depth of 7 in. Penetration, as judged by increase in available-phosphate content, appeared to be fairly slow, but comparatively more rapid in the wetter soil of plot 9 than in plot 7.

II. *Total phosphate*

The total phosphate of the various layers in the control plots remained fairly constant throughout the experiment.

The results of total-phosphate determinations suggest that treatment led to a considerable downward movement of phosphate; and some plots provide such evidence of penetration to a depth of 7 in. In other words, the total—as distinct from the available—phosphate may be increased to that depth, after the application of superphosphate. The rate of

penetration, as judged by increase of total phosphate, varied much with soil type.

(*a*) *Old Red Sandstone boulder clay*. Two months after the application of superphosphate there was an increase of total phosphate to a depth of 7 in. in the poorly drained soil of plot 1, to 5 in. in the freely drained soil of plot 3, but only to a depth of 3 in. in the acid freely drained soil of plot 5.

In plot 3 there were increases of total phosphate to the 7-in. layer 6 months after the application of superphosphate; but in the more acid soil of plot 5 there was no such suggestion of phosphate penetration below a depth of 5 in. even at the end of 3 years.

Judging by the total-phosphate figures, in the freely drained soils a high percentage of the phosphate applied appeared to be retained in the top 3 in. In the poorly drained soil the penetration to lower layers was much more marked. A comparison of the three plots, 3 years after the application of superphosphate, shows that in the freely drained soils of plots 3 and 5 the top 3–4 in. of soil have been raised in total-phosphate content, but lower layers have similar total-phosphate status to that found before the application of phosphate. In the poorly drained soil of plot 1 there was a considerable increase in total-phosphate content down to depths of 7 in. and probably deeper.

(*b*) *Littoral sands*. The total-phosphate figures suggest that applied phosphate moved downwards fairly rapidly, and possibly much of it was lost, especially under poor drainage conditions.

There was an almost rapid penetration (as judged by total-phosphate figures) in the slightly poorly drained soil of plot 7, but the amounts which underwent this quick translocation were small. Two months after the application of superphosphate there were small increases of total phosphate at all levels down to and including the 7-in. layer. A high percentage of the phosphate was, however, retained in the upper (0–3 in.) layers. Translocation of phosphate below about 3 in., so as to increase the amounts of total phosphate beyond those present at the end of the second month, appeared to be slow, but after 3 years cumulative movements in all layers down to a depth of 7 in. had increased their total phosphate by a considerable amount.

In the poorly drained soil of plot 9 the results are rather different from those obtained elsewhere. It will be noted that after 3 years the total phosphate of the various layers had almost reverted to the original values found before the application of superphosphate. There must therefore have been a considerable loss of phosphate by leaching. As in other centres, there was the tendency for phosphate to be retained in the upper layers.

It is reasonable to think that in a really badly drained soil there would be movement of phosphate of a kind which could hardly occur extensively in a well drained soil. The soil-solution conditions and the equilibrium between soil and soil solution would be different; and, in a soil continuously supplied with water, downward movement of phosphate might occur to an extent which would be nearly impossible in a soil frequently dried and re-wetted. The observed results suggest that some such mechanisms do indeed operate in poorly drained soils.

The role to be assigned to the organic matter and its concomitants is obscure. The pairs 7, 8 and 9, 10 did not differ significantly in percentage of organic matter (as measured by loss on ignition), but 9 and 10 are black and appear more humose than 7 and 8. It is possible that the more rapid leaching of phosphate in plot 9 may be associated with some 'mobilization' into which the organic matter enters.

TABLE 1

Results of Tests of Sampling Technique

A. *Available phosphate*

Depth of sampling (in.)	*Mg. of available* P_2O_5 *per 100 g. air-dry soil*						
	Sample					*Mean*	*Standard deviation*
	1	*2*	*3*	*4*	*5*		
0–1	20·2	19·4	20·5	18·4	20·0	19·7	±0·8
1–2	3·9	3·6	4·2	4·8	5·0	4·3	±0·6
2–3	2·3	2·3	2·0	2·3	4·1	2·6	±0·8
3–4	2·3	4·8	3·0	3·3	4·1	3·5	±1·0
4–5	2·3	4·5	2·3	2·3	3·6	3·0	±1·0
5–6	1·9	3·0	2·0	3·6	3·5	2·8	±0·8
6–7	2·0	1·1	2·7	3·0	3·7	2·5	±1·0

B. *Total phosphate*

Depth of sampling (in.)	*Mg. of total* P_2O_5 *per 100 g. air-dry soil*						
	Sample					*Mean*	*Standard deviation*
	1	*2*	*3*	*4*	*5*		
0–1	243	233	243	240	233	238	±5·1
1–2	153	151	159	154	159	156	±3·4
2–3	133	131	132	121	128	129	±4·9
3–4	116	116	129	119	127	122	±6·0
4–5	113	120	113	111	113	114	±3·4
5–6	108	108	112	116	106	110	±4·0
6–7	107	105	105	112	106	107	±2·9

Discussion

Available phosphate

The effect of applications of superphosphate, on grassland, on the available-phosphate status of the soil has been found to be most marked in the surface 2–3 in. This is in broad agreement with the results of other workers.

An investigation of the effects of natural drainage conditions, however, reveals that under wetter soil conditions the available phosphate was increased to a greater degree by the application of phosphate than where good drainage existed. Downward movement of available phosphate was also more marked in poorly drained soils. In the drier soils there was little, if any, increase in available phosphate below the 3–4-in. layer. In the wetter soils increases were found down to a depth of 7 in.

As might be expected, application of phosphate to the acid soil of

plot 5 had much less effect on the available-phosphate content than was found in other plots. Phosphate fixation in this soil must be very great. Increases in available phosphate in layers below 2 in. were almost negligible; and even in the upper layers the increase in percentage of available phosphate was not so great as in the less acid soil of plot 3.

In all centres the available-phosphate status of the upper layers gradually decreased, but the superphosphate dressing had, after 3 years, increased the available phosphate considerably to a depth of about 3 in.: this might be expected to give increased yields of pasture for a few years more. Measurement of pasture yields was not attempted, but differences in growth between the phosphate-treated and the control plots were always apparent.

Total phosphate

On the basis of available-phosphate contents, penetration of phosphate would not appear to be great. If, however, the total-phosphate results are taken as measures of penetration, it will be seen that under some conditions phosphate penetration must be considerable. The results also indicate that natural drainage conditions have a marked effect on the downward movement of phosphate.

Where the pH was over 6, i.e. in the Old Red Sandstone boulder clay soil, penetration to the 7-in. layer was quite marked in both poor and freely drained associates. The results suggest that penetration was more rapid and fixation less complete in the poorly drained associate. In the sandy loam (plot 7, slightly poorly drained; pH 6) there was also evidence of penetration of phosphate to depths of 7 in. and probably more, but under poorly drained conditions (plot 9) in this soil there appears to have been much loss of phosphate. It is an open question whether the losses arose through leaching or reduction under semi-anaerobic conditions.

The results are in agreement with what could be expected from influences of soil texture and structure. There was more rapid penetration in the light sandy loam than in the heavy boulder clay: both freely drained and of pH about 6.

Under acid conditions (plot 5) the greatest phosphate fixation occurred. This resulted in an accumulation of total phosphate in the top 2 or 3 in. of soil. Thus, under acid, freely drained conditions, phosphate was arrested in the surface layers.

Although there was considerable fixation of phosphate in the upper layers, the observations made on total phosphate suggest that soon after the application of superphosphate (this lapse of time depending, probably, on the rainfall and the evaporation balance) there was an initial rapid penetration of phosphate in solution into the lower layers. The amount of phosphate that was applied in these experiments is probably greater than that normally applied in grassland fertilization. It is conceivable that, after large applications of a soluble phosphate as top-dressing, considerable penetration—reflected in total phosphate—might occur before absorption and fixation had removed most of the phosphate from solution. Evidence in support of this supposition is strikingly given by plots 1 and 7. It is likely that large applications of phosphate will

promote greater penetration in depth than an equivalent amount applied in small doses. A similar conclusion was reached by Doak (1933) and Stephenson and Chapman (1931).

The penetration of phosphate, in inorganic form, probably depends largely on the phosphate-fixing power of the soil and on the relative solubility of the fixed phosphate compounds. Under the prevailing reducing conditions of poorly drained soils the phosphate may not be so firmly fixed as in the freely drained, and losses of phosphate might be expected to be greater in poorly drained soils.

Gaarder (1930) stated that in humid or semi-humid soils of high humus content, loss of phosphate may be very great. Results from plot 9 support the soundness of this contention. The percentage of organic matter in this soil was not very great (loss on ignition about 10 per cent.), but examination of the soil in the field suggested that it was of the peaty type, the colloids being nearly all organic. Three years after the application of superphosphate the phosphate status of this soil had almost reverted to its original level.

With each soil type, the comparison of poorly and freely drained associates was made in the same field of which the management and fertilizer treatment had probably been uniform over the whole area for many years. The initial total-phosphate content (before treatment) was greater in freely drained soils. This alone might be taken as showing that poorly drained soils are prone to suffer considerable removal of phosphate by leaching: a conclusion strongly reinforced by the later 'experimental' results discussed above.

Throughout the period of the experiment the total phosphate of all five control plots in both soil types remained fairly constant at their respective levels. This result agrees with the suggestion of Robinson and Jones (1927) and Doak (1933) that the phosphate in soil can be divided into two groups: (*a*) natural stable phosphorus compounds, and (*b*) the unstable phosphorus compounds of added dressings.

The available-phosphate results lend support to the contention of Wrenshall and McKibbin (1938) that the soluble phosphorus of untreated soil is an equilibrium quantity which probably does not vary significantly from year to year; and it represents a level approached in phosphate-treated soil after the effectiveness of the application has worn off. In some of the control plots there was an indication of phosphate penetration of residues of dressings applied prior to the experiment, but in general the available-phosphate contents (like the total-phosphate content) of the various layers remained constant.

The results of both total- and available-phosphate determinations are in agreement with the findings of Glentworth and Dion (1949). These workers found that in the surface layer (0–20 cm.) the acetic-soluble phosphorus was in general higher in poorly drained than freely drained associates. Their results also showed that total phosphate tended to be higher in freely drained associates.

The soil of Rothamsted Experimental Station in southern England is a heavy glacial clay with flints, but is naturally well drained.

Long-lasting residual manurial effects from the phosphate of farmyard manure and superphosphate have been observed (Anon., 1951) on arable soil there, which had been chalked to neutrality. The land in question had been under experiment up to 1901, having received liberal dressings of fertilizers for many years previously; from 1901 up to 1939 it was cropped mostly with cereals without fertilizers, and after 1939 with cereals receiving only ammonium sulphate.

In 1949, 'Crops on plots with farmyard manure or superphosphate residues contained over three times as much phosphoric acid as those without added phosphorus before 1901. The manurial residues were clearly shown by soil analysis. The contrasts were relatively great for readily soluble phosphoric acid (extracted by leaching with 0·5 M acetic acid)' (Anon., 1951).

These results appear to be in line with those of the present work: at least, in the freely drained Scottish soils there was no marked tendency for total 'available' (readily soluble) phosphate to fall actually or potentially within 3 years.

It is pertinent to note that on the Rothamsted cereal crops the residual effects from phosphate may have been reinforced and, as it were, emphasized by use of ammonium sulphate. It is probable that this salt increased the availability to crops of the residual phosphate through a direct solubilizing effect of acid produced by nitrification (cf. Tyagny-Ryadno, 1933), also by ionic or 'salt' effects of sulphate and nitrate.

The Rothamsted Report (Anon., 1951) made the point that 'the conventional low estimates of the residual value of phosphate fertilisers and the emphasis placed on phosphate fixation may derive in part from the failure of ordinary field experiments to measure small benefits maintained over long periods.' The present work appears to uphold the justness of this remark. It further indicates that while benefit from superphosphate applied as top-dressing to grassland can be expected for several years on freely drained and poorly drained soils alike, the mechanism of mobilization of phosphate, and the patterns of distribution of total and readily soluble phosphate with time at various depths in these unploughed soils, can be seen to differ with degree of freedom of natural drainage. (They are also likely to be altered by 'salt-action' arising from other fertilizers, including dressings of seaweed; also, near the sea, by wind-blown salt; and by eventual ploughing of the grassland.)

It is upon the 'unstable' phosphorus compounds formed after application of phosphate that the brunt of losses from leaching and/or reduction apparently falls. The present work brings out the importance of good drainage as a means towards lessening losses of phosphate given as fertilizer dressings. Though many workers have studied the lessening of the utility of applied phosphate that results from acidity, no published work is known to include comparative studies of the effects of drainage.

An agronomic conclusion to be drawn from the present experiments, in conjunction with the earlier results discussed above, is that poor

drainage will assist mobilization and can lead to good penetration of phosphate. Therefore, on any soil, grass can be expected to give an immediate response to a top-dressing of phosphate; thereafter the amounts of available phosphate can be expected to be greater at all depths (down to 7 in. at least) in poorly drained soils than in freely drained soils, but neither drainage class is likely to experience a deficiency of available phosphate for at least 3 years after the application of 240 lb. P_2O_5 per acre. Ultimately the poorly drained soils can be expected to incur actual loss of phosphate by drainage, whereas in the freely drained soils, which retain phosphate better, it can be expected that fixation will render a large proportion of the phosphate useless (unless a large amount of organic matter interferes with 'fixation' as ordinarily understood, or unless opportunity is given for a countervailing effect from salt-action to manifest itself upon the 'total phosphate').

A further agronomic consequence is an indication that currently held estimates may undervalue the residual effects that may be expected in some conditions after the application of phosphates.

The effect of sulphate

Only superphosphate was used as top-dressing in these experiments. It is tempting to suggest that the effects of good and poor drainage in apparently conserving and lessening, respectively, the utility of applied phosphate may—as far as the phosphate alone is concerned—hold also for other phosphatic fertilizers including farmyard manure and basic slag. Participation of other salts than phosphates cannot, however, be neglected. The nature of effects from fertilizer constituents which are water-soluble and can act concurrently with phosphate dressings given either separately or simultaneously in mixtures or 'compounds' must remain for the present largely speculative. Superphosphate contains a large proportion of the relatively soluble calcium sulphate, and through its effects on the ionic concentrations and conductance of the soil solution this sulphate must exercise a powerful influence on the mobility of phosphate. In soils of differing natural drainage, and hence of degree of aeration, the effects of added calcium or other sulphate will differ owing to the varied extents to which chemical reduction will allow the sulphate ion to enter into concentration equilibria.

These ionic effects of sulphate have not been investigated in the present work, but a hint about their importance can be obtained from the work of Aslyng (1951). He found that when a soil sample was shaken with a dilute solution of calcium chloride a small concentration of phosphate ions could be detected in the filtered solution: the more dilute the calcium chloride solution, the greater was the phosphate concentration. Further discussion does not seem likely to be very helpful in the absence of explicit data about the effect of sulphate in the field, but it is necessary to draw attention to the likelihood that effects from sulphate and other ions are important in studies of phosphate mobilization in the field. Wild (1950) gives a review of some investigations into the effects of salts on solubility of soil phosphate.

Summary

Drainage conditions had great influence during 3 years on the fate of phosphate (as superphosphate) applied to grassland.

When superphosphate was applied to a poorly drained soil the increase in 'available'-phosphate content of the soil was greater and of longer duration than when a similar dressing was applied to a freely drained soil. Fixation of phosphate appeared to be less rapid and less complete under poor drainage conditions.

Application of superphosphate to poorly drained soil resulted in increases in 'available' phosphate down to depths of 7 in. or more, but in freely drained soil increases of 'available' phosphate were not registered below depths of 3–4 in.

Downward movement of total phosphate was appreciable in poorly drained soil. This may account for losses of top-dressed phosphate from the surface layers. In freely drained soil, however, nearly all the applied phosphate was retained in the top 3 or 4 in. of soil.

No practical consequences from good and poor drainage in relation to phosphate were perceptible during 3 years, but the evidence indicates that 'fixation' may be less important than is usually believed. In freely drained soils a residual effect of phosphate may be appreciable.

Possible effects from the sulphate in superphosphate are discussed, and attention is drawn to the need for taking ionic effects and interactions into account in relation to phosphate availability.

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THE CONTRIBUTION TO SOIL ORGANIC MATTER AND NITROGEN FROM CEREAL RESIDUES AND UNDERSOWN CROPS

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Introduction

CONSIDERABLE concern is expressed from time to time about the maintenance of organic matter in the soil during periods of intensive cropping. It is, therefore, of importance as well as of interest to know how much may be contributed by the roots and stubble of cereal crops. In this connexion, account must also be taken of the possible influence of long stubble—such as is left by the combine harvester—for it is well known that the incorporation of straw into the soil will result in assimilation of available nitrogen by the soil microflora and a possible deficiency of nitrogen in the succeeding crop.

The composting of straw in bulk with nitrogenous compounds is frequently carried out, but straw may also be composted *in situ*, and a fairly common recommendation is to plough it in with enough nitrogenous fertilizer to overcome the danger of a shortage of available nitrogen for the next crop. Another method would be to plough in the straw with some leafy material grown with the cereal. It is indeed common practice in certain rotations to sow a grass seeds mixture with a cereal, and allow it to grow on, after the cereal has been harvested, to give a hay crop in the following year. The object of this investigation was to see whether it might be worth while to plough in an undersown crop with the cereal stubble—the undersown crop of clover or grass supplying nitrogen to achieve the same effect as a nitrogenous fertilizer.

There have been numerous investigations on the root development and root systems of different species of plants under various conditions. In the main, these investigations have been concerned with the manner in which the roots of a plant will ramify through the soil in search of nutrients and moisture—a matter of particular importance in semi-arid regions. The results have usually been recorded in the form of drawings and measurements of the root systems. There have been fewer observations on the actual weight of the roots, and those figures that have been published show wide variations. This is not surprising in view of the extent to which the growth of a crop and the development of its roots will depend upon the soil conditions, especially texture and moisture content, and the distribution of rainfall and temperature during the growing season. It would seem, however, that the dry matter of the roots and short stubble of most of the cereal and grass crops generally amounts to between 2,000 and 4,000 lb. per acre. Those figures are more closely examined below in the discussion of results.

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Experimental

Location. The experiments reported here were carried out in the Lothians on medium loam soils which were only slightly acid and were well supplied with plant nutrients. The normal annual precipitation is about 25 in. (35 in. at Boghall where two of the 1949 experiments were conducted), and in the four seasons concerned the rainfall during the growing period, from April to July inclusive, varied from 5·6 to 10·7 in.

Experimental design. The selected area under spring cereal was divided in April into a number of small plots on which Italian ryegrass or a clover was sown. In 1944 and 1945 the treatments were not randomized, but in 1947 and 1949 a Latin-square design was adopted with plots of 30 sq. yds. in area. After harvesting the cereal in August, a dressing of ammonium sulphate at the rate of 1 cwt. per acre was usually applied to half of the ryegrass plots. All the plots were sampled late in the autumn, except in the 1949 experiment when the sampling was delayed until March 1950.

To measure the effect of the residues on the next crop, the 1947 and 1949 plots were ploughed after sampling and sown out to a cereal whose yield of dry matter was determined. The effects of the same undersown crops were tested on a larger scale on each of two farms in 1949 with 16 plots of about $\frac{1}{8}$ acre arranged in 4 randomized blocks. Sampling of the residues was not carried out in these larger experiments, but half of each plot was ploughed during the autumn 1949 and the other half in spring 1950. A crop of oats was grown at each centre in 1950, harvested, threshed, and weighed.

Sampling. An undersown crop of clover or grass is frequently very patchy at harvest time, due partly to uneven tilth or moisture conditions at the time of sowing, and partly to local smothering by the cereal. Consequently the question of sampling the leaves and roots presents some difficulty. For the purpose of assessing the manurial value of the undersown crops it was considered preferable to obtain a reliable average value for the weight of roots from many small samples rather than a few precise figures by the careful separation of root material from large blocks of soil. Some preliminary observations indicated that coring would be the most expeditious method and that the error involved was of the order of 5 or 10 per cent. of the mean of 10 or 12 cores.

The selection for coring of areas where there is a good growth of crop is, of course, subject to the criticism that the sampling variance is of doubtful validity, but it does give a theoretical estimate of what might be regarded as the maximum amounts of root and leaf over a uniform area. This method was therefore adopted in seasons 1944 and 1945 on single plots. In seasons 1947 and 1949, however, when a Latin-square design was used, each plot of 30 sq. yds. was divided into 5 strips and 2 cores, located by random numbers, were taken from each strip. A statistical analysis of the results was thus possible. The treatments were red clover, Italian ryegrass, Italian ryegrass to which nitrogen was added after harvest, and control.

The tool employed for sampling was an ordinary golf-course corer

of internal diameter 3·95 in. and length about 4·5 in. With this instrument the cores are pushed out by foot action on a movable plate set inside the cylinder, and it is possible to take out two or three cores to increasing depths at the same place.

Washing. Each core was placed in a cylindrical cage made of perforated zinc, with holes 1·5 mm. in diameter, and broken up by a jet of water. The cage was then agitated under water, which brought about a fairly complete separation of soil from roots and leaves, and the residue in the cylinder was washed on to a 2-mm. sieve from which the larger stones were removed by hand. Then followed a succession of beaker washings by decantation, the liquid being poured through a 100-mesh sieve until the vegetable matter was as free as possible from soil contamination. This treatment did not remove the soil completely, however, some hard particles being held firmly by the roots. A correction for this mineral matter was made in the subsequent analysis. The root and top material was dried at 100° C. and weighed, and the entire mass was then digested in a kjeldahl flask. After digestion, the insoluble residue of mineral matter was collected, dried, and weighed, and subtracted from the original dry matter. The result is recorded in the tables as organic matter. It amounted to between 80 and 90 per cent. of the total dry matter and although it is only on approximation to the organic matter, because not all the mineral matter was insoluble in the sulphuric acid, it carries a correction for a large portion of the soil contamination. The nitrogen in solution was determined and computed as a percentage of this organic matter.

Results

The amount of roots found in the layer of soil 4·5 to 9 in. below the surface was very small and the weights recorded throughout are for the surface 4·5 in. In 1944 and 1945 the vegetable matter from every fifth core was separated before analysis into roots and tops (straw, leaves and stems) in order to find what proportions of the organic matter came from these parts of the plants. The results are summarized in Table 1 and show that the tops contributed significantly more than the roots in the cases of trefoil and white clover but not in the cases of ryegrass and red clover.

According to Goedewaagen and Schuurman (1950), the weight of roots is on the average only about 17 per cent. of the whole plant, but the ratio of shoot to root is liable to be influenced by fertilizer treatment. Pinck and Allison (1947) found that almost 40 or 45 per cent. of the dry matter and nitrogen in Sudan grass was in the roots, but that the application of a nitrogenous fertilizer reduced the figures to about 33 per cent. In the present investigation the values were of course subject to the recovery of the crop between cutting and sampling.

In the first three seasons the cores were taken in November, and the results in Table 2 show that the amount of organic matter from undersown crop and stubble varied from about 25 to 55 cwt./acre; the cereal stubble and roots of the control plots gave a figure lying between 13 and

TABLE 1

Organic Matter and Nitrogen in Tops and Roots

Crop and number of cores	*Organic matter (g. per core)**		*Nitrogen (mg. per core)*	
	Tops	*Roots*	*Tops*	*Roots*
Trefoil (10)	2·47±0·31	1·29±0·15	74·6±9·8	27·4±3·1
Ryegrass (10)	1·63±0·19	1·66±0·21	38·7±5·4	25·1±3·3
Stubble only (10)	1·42±0·12	0·89±0·07	8·8±0·7	11·0±1·1
Red clover (5)	2·34±0·51	2·56±0·48	56·9±10·0	57·0±10·8
White clover (5)	2·32±0·24	1·18±0·30	54·4±4·2	23·8±8·9
Ryegrass (5)	1·59±0·43	1·52±0·38	22·5±2·9	19·6±3·8
Stubble only (5)	0·75±0·24	0·74±0·16	4·9±1·3	7·7±1·0

* 1 g. per core is equivalent to 1,128 lb. per acre.

TABLE 2

Organic Matter and Nitrogen in Undersown Crop and Cereal Stubble Residues

Crop and number of cores	*Organic matter (lb. per acre)*	*Total nitrogen (lb. per acre)*	% N *in O.M.*
Sampled Nov. 1944			
Trefoil (50)	3,930±169	98±4·5	2·54±0·07
Ryegrass (50)	3,660±158	65±2·7	1·83±0·06
Stubble only (50)	2,810±124	22±0·9	0·82±0·06
Sampled Nov. 1945			
Red clover (25)	5,450±328	111±8·2	2·06±0·09
White clover (25)	4,140±192	86±4·0	2·11±0·02
Ryegrass (25)	2,970±226	42±2·3	1·50±0·06
Ryegrass+N (25)	3,140±147	38±2·3	1·21±0·06
Stubble only (25)	1,500±271	13±1·1	1·21±0·10
Sampled Nov. 1947			
Red clover (40)	5,090±260	122±8·0	2·42±0·10
Ryegrass (40)	4,610±248	45±2·4	1·01±0·03
Ryegrass+N (40)	6,080±293	67±3·7	1·17±0·06
Stubble only (40)	2,520±192	26±1·5	0·99±0·04
Sampled Mar. 1950			
Red clover (40)	2,120±127	45±2·9	2·16±0·10
Ryegrass (40)	2,830±152	44±2·1	1·59±0·05
Ryegrass+N (40)	2,310±119	40±2·4	1·77±0·04
Stubble only (40)	1,670±86	34±1·8	2·07±0·02

25 cwt./acre, but this is likely to vary a good deal according to the length of the stubble left by the harvesting machine.

It was impracticable to separate the cereal stubble and roots from the plants of the undersown crop and it was not considered justifiable to estimate the figures for the undersown crop by deducting the cereal residue of the control plots, partly because there was a certain amount of weed growth between harvest and coring, particularly on the control

plots, and partly because the yield of a cereal is usually reduced by an undersown crop. The cereal crop was weighed at harvest time only in 1947 and the mean yield was greatest on the control plots. This result was in agreement with the conclusions reached by Lyon (1936) after a long-term investigation of mixed crops.

In 1947 the plots were ploughed in November and rye was sown in 1948 and cut three times during the season. The average total weights of dry matter and nitrogen from the different treatments are given in Table 3. The plots of the 1949 experiment (Table 2) were not ploughed until March 1950, and the coring was delayed until then so that the samples might be representative of the material ploughed in. During the winter there had been many periods of low temperatures (temperatures below 30·4° F. were recorded on 60 days) which were no doubt responsible for the relatively small amount of clover that survived. At any rate the contribution by clover in the 1949 experiment was much smaller than in previous years. Barley was sown and cut soon after heading, when still green. The results are shown in Table 3.

With respect to the crops of oats on the randomized-block experiments in 1950, the yields from the autumn-ploughed portions of the plots were generally higher than those from the spring-ploughed portions, but the differences were of doubtful significance and the two sets of results are combined in Table 3. The results obtained at the two farms (Boghall and Riggonhead) were remarkably similar.

TABLE 3

Average Dry Matter and Nitrogen (lb. per acre) in Cereals from Plots undersown in the Previous Year and ploughed under

Following crop	*Red clover*	*Ryegrass*	*Ryegrass +N*	*Control*	*S.E. of mean*
3 cuts of rye, 1948 (1)					
Dry matter	5,380	2,710	3,120	3,260	±242
Nitrogen	81	38	44	47	± 3·9
% N	1·5	1·4	1·4	1·4	..
Barley cut at heading, 1950 (2)					
Dry matter	3,050	1,310	1,950	1,680	± 90
Nitrogen	52	21	35	30	± 3·2
% N	1·7	1·5	1·7	1·7	..
Oats, grain, 1950 (3)					
Dry matter	2,540	1,680	1,890	1,670	±100
Nitrogen	34	23	25	21	± 1·1
% N	1·3	1·3	1·3	1·3	..
Oats, grain, 1950 (4)					
Dry matter	2,620	1,680	2,140	1,630	± 73
Nitrogen	44	27	33	24	± 1·2
% N	1·7	1·6	1·6	1·4	..

(1) From plots sampled Nov. 1947, Table 2.
(2) From plots sampled Mar. 1950, Table 2.
(3) From 4 randomized blocks of approximately $\frac{1}{4}$-acre plots at Boghall.
(4) From 4 randomized blocks of approximately $\frac{1}{8}$-acre plots at Riggonhead.

Discussion of Results

The influence of environment upon the habit and extent of root growth is well demonstrated in the results obtained by Weaver (1920), who studied the root development in grassland at numerous places between the Missouri river and the Rocky Mountains. Under the conditions of soil, temperature, and evaporation existing in that region the roots of red clover commonly reached 3 or 4 ft. in 2 or 3 months after sowing. In contrast, Farris (1934) found that in the more humid region of New Jersey the bulk of the roots of different strains of red clover were to be found in the top 8 in. of soil, 7 months after sowing, although there was some penetration to 12 or 14 in. He assumed that the development of extensive root systems was not stimulated under the prevailing conditions of ample moisture and supplies of nutrients. Lamba, Ahlgren, and Muckenhirn (1949) separated and weighed the roots in 1-ft.-square columns from pure strains of clovers and grasses grown on different soil types in Wisconsin, and found large differences between species on the same soil and also in any one species grown on different soils. For example, 5 months after sowing on Miami silt loam a medium red clover had 2,144 lb. of roots per acre in the surface 8 in. and 100 lb. in the layer 8 to 16 in.; the corresponding figures for lucerne, brome-grass, and timothy were respectively 3,247 and 764, 1,648 and 185, 1,064 and trace. Lamba *et al.* observed that the penetration of the roots was greatly influenced by the acidity, moisture conditions, and aeration of the soil and that, of the total weights of roots, much larger proportions were located in the surface 8 in. of soil with clover and timothy than with lucerne and brome-grass. Gist and Smith (1948) recorded the same difference in the habits of brome-grass and timothy.

Goedewaagen and Schuurman (1950) have summarized the figures for the yields of roots and stubble in the surface 8 in. from several European investigations on various crops. There are striking variations both within and between crops, but some of the average values in lb. per acre are 1,250 for barley and white clover, 2,500 for oats, and 1,960 for red clover. The yields of clover roots increased with the age of the plants. In an experiment in which red clover was sown in April with a cover crop of barley, the weight of clover roots in September was only 360 lb. per acre. With 11 crops whose roots penetrated to a depth of about 40 in., 74 per cent. of the total mass of roots appeared on the average in the surface 8 in., but this figure varied from 55 to 95 per cent. In the case of grassland, especially after the first year, about 70 per cent. of the roots were found in the surface 2 in. of soil, even when some roots penetrated 30 or 40 in., and the total weight of roots was higher than for grain crops, the annual production of grass roots being probably about 4,500 lb. per acre. In general, the weight of roots was increased by improving the fertility of the soil.

These observations make it quite clear that the contribution of organic matter to the soil in the form of crop roots and residues is liable to vary considerably even when allowance is made for different techniques in making the appropriate measurements.

As mentioned above, the results recorded in Table 2 are for the surface $4\frac{1}{2}$ in. of soil, and include the bulk but not the whole of the roots. The 1944 and 1945 results are also simply comparisons from single plots, but they are in general accord with the results obtained in 1947 and 1949 which have been fully analysed. In no case, in 1947, was the variance ratio 'between strips' to 'within strips' significantly different from unity, so that the variance between strips could be assumed to be equal to the variance within strips and all the results could be pooled to calculate the variances for treatments. When the treatment means are compared with one another it is found that, in the case of organic matter, 'Ryegrass+N' is significantly the largest and 'stubble only' the smallest; there is no significant difference between the other two. In the case of total nitrogen, each treatment mean differs significantly from all the others. In the results for percentage of nitrogen, the 'clover' is far superior to all the others, and the 'Ryegrass+N' is superior to the remaining two treatments which do not differ significantly. There is not much difference in the coefficients of variation for the four treatments so that the heterogeneity did not depend to any extent upon the particular treatment. There was a small but significant negative correlation, for a given treatment, between organic matter and percentage nitrogen, but the average value of the regression coefficient ($-0{\cdot}071 \pm 0{\cdot}016$), though significant, had a rather large standard error and could not be used in practice to estimate the total nitrogen from the yield of organic matter.

In the 1949 experiment the plots were not cored until March 1950, and this was no doubt responsible to a large extent for a set of results that differred substantially from those in 1947. The smallest contribution again came from the vegetation on the control plots, but a good deal of the straw had doubtless decomposed during the winter and been replaced by weeds which probably account for the relatively high percentage of nitrogen. It was obvious that much of the clover had not survived the frequent spells of low temperatures during the winter. The highest yield of organic matter came from the untreated 'Ryegrass' plots, whilst the 'Ryegrass+nitrogen' and 'Clover' plots yielded substantially the same amounts. The reason for the adverse effect of the nitrogen fertilizer on the ryegrass can only be surmised.

It is of interest to consider the following average results for 3 years, when clover and ryegrass were directly compared, with the average figures for a dressing of 10 tons of farmyard manure.

Residues after cereal harvest	*Cereal alone*	*Cereal +ryegrass*	*Cereal +red clover*	*10 tons F.Y.M.*
Organic matter (lb. per acre) .	1,900	3,470	4,220	3,800
Nitrogen (lb. per acre) . .	24	44	93	110
% N in O.M. . . .	1·26	1·27	2·20	3

The farmyard manure supplies just about the same amount of organic matter as the ryegrass and clover residues, but it is richer in nitrogen. Since it is the proportion of the nitrogen in the organic residues rather than the total amount that determines how much nitrogen will be available

for the next crop, there was reason to expect that the stubble-clover residues would be more beneficial than the others in the following year.

The results in Table 3 for the 1948 and 1950 cereal crops grown on the 1947 and 1949 plots respectively lend support to this argument. The analysis of the 1948 figures shows that, both as regards dry matter and nitrogen, there is a highly significant difference between the clover plots and the other three treatments, but none amongst these three. In the 1950 barley experiment the yields of dry matter and nitrogen from the clover plots were again far superior to those from any of the other three treatments while the 'Ryegrass+N' was significantly better at the 5 per cent. level than the 'Ryegrass'. Even the control was significantly better in dry-matter production than the 'Ryegrass' at the 5 per cent. level.

The two additional large randomized-block experiments carried out in 1950, on plots undersown in 1949 but not sampled, confirm the Latin-square results of 1948 and 1950. In the Boghall experiment (3), the clover was again far superior to the other three treatments for both dry matter and nitrogen produced in the grain. The other three treatments did not differ significantly from each other in dry-matter production, but the difference in nitrogen between the 'Ryegrass+N' and the control was just significant at the 5 per cent. level. In the Riggonhead experiment (4), the clover treatment was superior in dry matter and nitrogen to all the other treatments and the 'Ryegrass+N' was superior to the remaining two treatments, which were not significantly different from each other.

It is noteworthy that in each of these four experiments the treatment did not exert an appreciable influence upon the percentage of nitrogen in the crop. The uptake of nitrogen was therefore very closely related to the crop yield. It would be hazardous, however, to calculate what proportion of the nitrogen in the residues became available to the following crops because there must almost certainly have been some change in the carbon:nitrogen ratio of the residues during the winter months. The outstanding superiority of the clover residues in every experiment is probably connected with their relatively high nitrogen content, but other nutrient elements, such as calcium, which is normally higher in legumes than in grasses, might easily play a part in the speed of decomposition of the organic matter.

The general conclusions that may be drawn from the experiments are that the organic residues from a cereal crop are considerably augmented by undersowing a grass or a clover and that the clover residues are much richer in nitrogen and are very effective in increasing the yield of the next crop whereas ryegrass residues have not much influence on the next crop unless they are treated with a nitrogenous fertilizer. A good deal of experimental work would be required to establish whether the value of the increase in crop yield would in general be greater than the combined cost of undersowing and reduction in yield of the undersown cereal by competition from the clover.

We should like to record that the late Dr. A. Cunningham initiated these investigations and that we have been much indebted to Dr. D. N. Lawley for assistance in the statistical examination of the results and to Mr. G. R. White for help in the field.

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